

\$%^STN;HighlightOn= ***;HighlightOff=*** ;

Connecting via Winsock to STN

Welcome to STN International! Enter x:X

LOGINID:SSPTABAM1797

PASSWORD:

TERMINAL (ENTER 1, 2, 3, OR ?):2

* * * * * Welcome to STN International * * * * *

NEWS	1		Web Page for STN Seminar Schedule - N. America
NEWS	2	AUG 10	Time limit for inactive STN sessions doubles to 40 minutes
NEWS	3	AUG 18	COMPENDEX indexing changed for the Corporate Source (CS) field
NEWS	4	AUG 24	ENCOMPLIT/ENCOMPLIT2 reloaded and enhanced
NEWS	5	AUG 24	CA/CAPplus enhanced with legal status information for U.S. patents
NEWS	6	SEP 09	50 Millionth Unique Chemical Substance Recorded in CAS REGISTRY
NEWS	7	SEP 11	WPIDS, WPINDEX, and WPIX now include Japanese FTERM thesaurus
NEWS	8	OCT 21	Derwent World Patents Index Coverage of Indian and Taiwanese Content Expanded
NEWS	9	OCT 21	Derwent World Patents Index enhanced with human translated claims for Chinese Applications and Utility Models
NEWS	10	NOV 23	Addition of SCAN format to selected STN databases
NEWS	11	NOV 23	Annual Reload of IFI Databases
NEWS	12	DEC 01	FRFULL Content and Search Enhancements
NEWS	13	DEC 01	DGENE, USGENE, and PCTGEN: new percent identity feature for sorting BLAST answer sets
NEWS	14	DEC 02	Derwent World Patent Index: Japanese FI-TERM thesaurus added
NEWS	15	DEC 02	PCTGEN enhanced with patent family and legal status display data from INPADOCDB
NEWS	16	DEC 02	USGENE: Enhanced coverage of bibliographic and sequence information

NEWS EXPRESS MAY 26 09 CURRENT WINDOWS VERSION IS V8.4,
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* * * * * STN Columbus * * * * *

FILE 'HOME' ENTERED AT 12:17:04 ON 05 DEC 2009

=>

=> file registry

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

0.22

0.22

FILE 'REGISTRY' ENTERED AT 12:17:20 ON 05 DEC 2009

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STRUCTURE FILE UPDATES: 4 DEC 2009 HIGHEST RN 1196030-76-8

DICTIONARY FILE UPDATES: 4 DEC 2009 HIGHEST RN 1196030-76-8

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REGISTRY includes numerically searchable data for experimental and
predicted properties as well as tags indicating availability of
experimental property data in the original document. For information
on property searching in REGISTRY, refer to:

<http://www.cas.org/support/stngen/stndoc/properties.html>

=> s 110-98-5/rn

L1 1 110-98-5/RN

=> d L1

L1 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN

RN ***110-98-5*** REGISTRY

ED Entered STN: 16 Nov 1984

CN 2-Propanol, 1,1'-oxybis- (CA INDEX NAME)

OTHER CA INDEX NAMES:

CN 2-Propanol, 1,1'-oxydi- (6CI, 7CI, 8CI)

OTHER NAMES:

CN 1,1'-Dimethyldiethylene glycol

CN 1,1'-Oxydi-2-propanol

CN Bis(2-hydroxypropyl) ether

CN NSC 8688

MF C6 H14 O3

CI COM

LC STN Files: ANABSTR, AQUIRE, BEILSTEIN*, CA, CAPLUS, CASREACT,
CHEMCATS,

CHEMLIST, CSCHEM, HSDB*, IFICDB, IFIPAT, IFIUDB, MSDS-OHS,
RTECS*,

SPECINFO, TOXCENTER, ULIDAT, USPAT2, USPATFULL, USPATOLD

(*File contains numerically searchable property data)
Other Sources: DSL**, EINECS**, TSCA**
(*Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 1 in file .gra /

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

134 REFERENCES IN FILE CA (1907 TO DATE)
4 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
135 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> s 25265-71-8/rn
L2 1 25265-71-8/RN

=> d L2

L2 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN
RN ***25265-71-8*** REGISTRY
ED Entered STN: 16 Nov 1984
CN Propanol, oxybis- (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Dipropylene glycol (6CI)
OTHER NAMES:
CN ADK DPG-RF
DR 25322-23-0, 75047-14-2, 78644-49-2, 27941-90-8, 27941-91-9, 28678-
26-4,
30370-61-7
MF C6 H14 O3
CI IDS, COM
LC STN Files: AGRICOLA, ANABSTR, AQUIRE, BIOSIS, BIOTECHNO, CA,
CAPLUS,
CASREACT, CBNB, CHEMCATS, CHEMLIST, CHEMSAFE, CIN, CSCHEM, CSNB,
DETERM*, EMBASE, HSDB*, IFICDB, IFIPAT, IFIUDB, MEDLINE, MSDS-
OHS,
PIRA, PROMT, RTECS*, TOXCENTER, TULSA, ULIDAT, USPAT2, USPATFULL,
USPATOLD
(*File contains numerically searchable property data)
Other Sources: DSL**, EINECS**, TSCA**
(*Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 2 in file .gra /

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

4812 REFERENCES IN FILE CA (1907 TO DATE)
684 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
4820 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> s 7320-37-8/rn
L3 1 7320-37-8/RN

=> d L3

L3 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN
RN ***7320-37-8*** REGISTRY
ED Entered STN: 16 Nov 1984
CN Oxirane, 2-tetradecyl- (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Hexadecane, 1,2-epoxy- (6CI, 7CI, 8CI)
CN Oxirane, tetradecyl- (9CI)
OTHER NAMES:
CN 1,2-Epoxyhexadecane
CN 1,2-Epoxyhexadecene
CN 1,2-Hexadecene epoxide
CN 1,2-Hexadecylene oxide
CN 1-Hexadecene oxide
CN Cyracure UVR 6216
CN Hexadecylene oxide
CN Tetradecyloxirane
CN UVR 6216
CN Vikolox 16
DR 151284-10-5
MF C16 H32 O
CI COM
LC STN Files: ANABSTR, BEILSTEIN*, BIOSIS, CA, CAPLUS, CASREACT,
CHEMCATS,
CHEMINFORMRX, CHEMLIST, CSCHEM, CSNB, HSDB*, IFICDB, IFIPAT,
IFIUDB,
PIRA, PROMT, RTECS*, SPECINFO, TOXCENTER, USPAT2, USPATFULL,
USPATOLD
(*File contains numerically searchable property data)
Other Sources: EINECS**, NDSL**, TSCA**
(**Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 3 in file .gra /

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

345 REFERENCES IN FILE CA (1907 TO DATE)
105 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
345 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> s 280-57-9/rn
L4 1 280-57-9/RN

=> d L4

L4 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN
RN ***280-57-9*** REGISTRY
ED Entered STN: 16 Nov 1984
CN 1,4-Diazabicyclo[2.2.2]octane (CA INDEX NAME)
OTHER NAMES:
CN 1,4-Ethylenepiperazine
CN 33LV
CN A 33
CN Activator 105E
CN AE 33
CN Bicyclo[2.2.2]-1,4-diazaoctane

CN D 33LV
 CN Dabco
 CN Dabco 33LV
 CN Dabco 3LV
 CN DABCO Crystal
 CN Dabco Crystalline
 CN Dabco L 1202
 CN Dabco S 25
 CN Jeffcat TD 100
 CN Kaolizer 31
 CN L 33
 CN L 33E
 CN LC 96003
 CN LV 33
 CN Minico L 1020
 CN N,N'-endo-Ethylenepiperazine
 CN Niax A 33
 CN NSC 56362
 CN PC CAT TD 33
 CN PC-TD
 CN Polycat 33LV
 CN TD 100
 CN TED
 CN TEDA
 CN Teda L 33
 CN Tegamine 33
 CN Tego Amine
 CN Tegoamin 33
 CN Texacat TD 100
 CN Texacat TD 33
 CN Thancat TD 33
 CN Thancat TD 33A
 CN Toral SM 2
 CN Toyocat L 33
 CN Toyocat TEDA L 33
 CN Triethylenediamine
 DR 746642-46-6, 903524-95-8, 165724-47-0, 23790-33-2, 101484-19-9,
 150605-01-9, 88935-43-7, 203072-11-1, 309955-09-7
 MF C6 H12 N2
 CI COM, RPS
 LC STN Files: AGRICOLA, ANABSTR, AQUIRE, BEILSTEIN*, BIOSIS,
 BIOTECHNO, CA,
 CAPLUS, CASREACT, CBNB, CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN,
 CSCHEM,
 CSNB, DETHERM*, EMBASE, ENCOMPLIT, ENCOMPLIT2, ENCOMPPAT,
 ENCOMPPAT2,
 GMELIN*, HSDB*, IFICDB, IFIPAT, IFIUDB, MEDLINE, MRCK*, MSDS-OHS,
 PIRA,
 PROMT, RTECS*, SPECINFO, SYNTHLINE, TOXCENTER, ULIDAT, USPAT2,
 USPATFULL, USPATOLD
 (*File contains numerically searchable property data)
 Other Sources: DSL**, EINECS**, TSCA**
 (**Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 4 in file .gra /

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

6696 REFERENCES IN FILE CA (1907 TO DATE)
321 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
6716 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> file caplus uspatfull
COST IN U.S. DOLLARS

	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	33.64	33.86

FILE 'CAPLUS' ENTERED AT 12:49:23 ON 05 DEC 2009
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=> s L4 and L3 and L2
L5 1 L4 AND L3 AND L2

=> d L5 ibib hit

L5 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2005:1027004 CAPLUS <<LOGINID::20091205>>
DOCUMENT NUMBER: 143:328922
TITLE: Hydrocarbon desulfurization with mercaptan
removal by
treatment with alicyclic tertiary amines and
nucleophilic acceptors
INVENTOR(S): Schield, John A.; Cappel, Weldon John
PATENT ASSIGNEE(S): Baker Hughes Incorporated, USA
SOURCE: PCT Int. Appl., 23 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
-----	----	-----	-----	-----
WO 2005087899	A1	20050922	WO 2004-US4011	
20040211				
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE,			

ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI,
SK,
TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN,
TD, TG
CA 2554548 A1 20050922 CA 2004-2554548
20040211
EP 1713885 A1 20061025 EP 2004-710238
20040211
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC,
PT,
IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, SK
US 20070142244 A1 20070621 US 2006-588341
20060803
PRIORITY APPLN. INFO.: WO 2004-US4011 W
20040211
ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OTHER SOURCE(S): MARPAT 143:328922
REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE
FOR THIS

RECORD. ALL CITATIONS AVAILABLE IN THE RE
FORMAT

IT ***280-57-9*** , 1,4-Diazabicyclo[2.2.2]octane 3001-72-7,
1,5-Diazabicyclo[4.3.0]non-5-ene 6674-22-2,
1,8-Diazabicyclo[5.4.0]undec-7-ene
RL: CPS (Chemical process); PEP (Physical, engineering or chemical
process); PROC (Process)
(hydrocarbon desulfurization with mercaptan removal by treatment
with
alicyclic tertiary amines and nucleophilic acceptors)
IT ***25265-71-8*** , Dipropylene glycol
RL: NUU (Other use, unclassified); USES (Uses)
(hydrocarbon desulfurization with mercaptan removal by treatment
with
alicyclic tertiary amines and nucleophilic acceptors)
IT 463-73-0D, Chloroformic acid, compds. 2817-45-0D, Phosphoramidic
acid,
compds. ***7320-37-8*** , 1,2-Epoxyhexadecane 19270-07-6D,
Cyanofomic acid, compds.
RL: CPS (Chemical process); PEP (Physical, engineering or chemical
process); PROC (Process)
(nucleophilic acceptors; hydrocarbon desulfurization with
mercaptan
removal by treatment with alicyclic tertiary amines and
nucleophilic
acceptors)

=> s L4 and L2
L6 84 L4 AND L2

=> s L6 and epoxide
L7 11 L6 AND EPOXIDE

=> d L7 ti

L7 ANSWER 1 OF 11 CAPLUS COPYRIGHT 2009 ACS on STN
TI Hydrocarbon desulfurization with mercaptan removal by treatment
with
alicyclic tertiary amines and nucleophilic acceptors

=> d L7 1-11 ti

L7 ANSWER 1 OF 11 CAPLUS COPYRIGHT 2009 ACS on STN
TI Hydrocarbon desulfurization with mercaptan removal by treatment
with
alicyclic tertiary amines and nucleophilic acceptors

L7 ANSWER 2 OF 11 CAPLUS COPYRIGHT 2009 ACS on STN
TI Flame retardant, additive compositions, and flame retardant
polyurethanes

L7 ANSWER 3 OF 11 CAPLUS COPYRIGHT 2009 ACS on STN
TI Molding of polyisocyanurate heat-resistant resins

L7 ANSWER 4 OF 11 CAPLUS COPYRIGHT 2009 ACS on STN
TI Curable epoxy resin containing molding compositions

L7 ANSWER 5 OF 11 USPATFULL on STN
TI System, method and composition for adhering preformed
thermoplastic
traffic control signage to pavement

L7 ANSWER 6 OF 11 USPATFULL on STN
TI Method of producing flexible laminates

L7 ANSWER 7 OF 11 USPATFULL on STN
TI SELF-PHOTOINITIATING MULTIFUNCTIONAL URETHANE OLIGOMERS
CONTAINING
PENDANT ACRYLATE GROUPS

L7 ANSWER 8 OF 11 USPATFULL on STN
TI Flame retardant, additive compositions, and flame retardant
polyurethanes

L7 ANSWER 9 OF 11 USPATFULL on STN
TI Silicon and phosphorus containing compositions

L7 ANSWER 10 OF 11 USPATFULL on STN
TI Curable epoxy resin containing molding compositions

L7 ANSWER 11 OF 11 USPATFULL on STN
TI Polyepoxide curing by polymercaptans catalyzed by dimethylamino
alkyl
ethers

=>
=>

---Logging off of STN---

=>
Executing the logoff script...

=> LOG Y

COST IN U.S. DOLLARS	SINCE FILE	TOTAL
FULL ESTIMATED COST	ENTRY	SESSION
	65.15	99.01

STN INTERNATIONAL LOGOFF AT 13:28:22 ON 05 DEC 2009

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PASSWORD:

TERMINAL (ENTER 1, 2, 3, OR ?):2

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NEWS	7	SEP 11	WPIDS, WPINDEX, and WPIX now include Japanese FTERM thesaurus
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NEWS	12	DEC 01	FRFULL Content and Search Enhancements
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NEWS	15	DEC 02	PCTGEN enhanced with patent family and legal status display data from INPADOCDB
NEWS	16	DEC 02	USGENE: Enhanced coverage of bibliographic and sequence information

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* * * * * STN Columbus * * * * *

FILE 'HOME' ENTERED AT 13:54:24 ON 05 DEC 2009

=> file registry

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	0.22	0.22

FILE 'REGISTRY' ENTERED AT 13:54:38 ON 05 DEC 2009

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DICTIONARY FILE UPDATES: 4 DEC 2009 HIGHEST RN 1196030-76-8

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REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

<http://www.cas.org/support/stngen/stndoc/properties.html>

=> s 6674-22-2/rn

L1 1 6674-22-2/RN

=> d L1

L1 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN

RN ***6674-22-2*** REGISTRY

ED Entered STN: 16 Nov 1984

CN Pyrimido[1,2-a]azepine, 2,3,4,6,7,8,9,10-octahydro- (CA INDEX NAME)

OTHER NAMES:

CN 1,8-Diaza-7-bicyclo[5.4.0]undecene

CN 1,8-Diazabicyclo[5.4.0]undec-7-ene

CN 1,8-Diazabicyclo[5.4.0]undecene-7

CN 2,3,4,6,7,8,9,10-Octahydropyrimido[1,2-a]azepine

CN Alcanpoudre DBU 70-3KG

CN Amicure DBUE

CN Dabco DBU

CN DBU
CN NSC 111184
CN NSC 230466
CN Polycat DBU
CN U-CAT SA 851
DR 51301-56-5, 69722-76-5, 78995-63-8, 83329-50-4, 31171-04-7, 41015-70-7
MF C9 H16 N2
CI COM
LC STN Files: ANABSTR, BEILSTEIN*, BIOSIS, CA, CAPLUS, CASREACT, CHEMCATS,
CHEMINFORMRX, CHEMLIST, CIN, CSCHEM, GMELIN*, IFICDB, IFIPAT, IFIUDB,
MEDLINE, MSDS-OHS, SPECINFO, TOXCENTER, USPAT2, USPATFULL, USPATOLD
(*File contains numerically searchable property data)
Other Sources: DSL**, EINECS**, TSCA**
(**Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 5 in file .gra /

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

4005 REFERENCES IN FILE CA (1907 TO DATE)
152 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
4035 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> s 3001-72-7/rn
L2 1 3001-72-7/RN

=> d L2

L2 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN
RN ***3001-72-7*** REGISTRY
ED Entered STN: 16 Nov 1984
CN Pyrrolo[1,2-a]pyrimidine, 2,3,4,6,7,8-hexahydro- (CA INDEX NAME)
OTHER NAMES:
CN 1,5-Diazabicyclo[4.3.0]non-5-ene
CN 1,5-Diazabicyclo[4.3.0]nonene-5
CN 1,5-Diazobicyclo[4.3.0]non-5-ene
CN 2,3,4,6,7,8-Hexahydropyrrolo[1,2-a]pyrimidine
CN DBN
CN DBN (heterocycle)
CN NBU
CN NSC 118106
DR 25986-32-7, 312727-86-9
MF C7 H12 N2
CI COM
LC STN Files: ANABSTR, BEILSTEIN*, BIOSIS, CA, CAPLUS, CASREACT, CHEMCATS,
CHEMINFORMRX, CHEMLIST, CSCHEM, GMELIN*, IFICDB, IFIPAT, IFIUDB,
MEDLINE, MSDS-OHS, SPECINFO, SYNTHLINE, TOXCENTER, USPAT2, USPATFULL,
USPATOLD
(*File contains numerically searchable property data)

Other Sources: EINECS**
(**Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 6 in file .gra /

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1103 REFERENCES IN FILE CA (1907 TO DATE)
44 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
1110 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> s 280-57-9/rn
L3 1 280-57-9/RN

=>
=> file caplus uspatfull
COST IN U.S. DOLLARS SINCE FILE TOTAL
ENTRY SESSION
FULL ESTIMATED COST 17.54 17.76

FILE 'CAPLUS' ENTERED AT 14:11:39 ON 05 DEC 2009
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FILE 'USPATFULL' ENTERED AT 14:11:39 ON 05 DEC 2009
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=> s L1 OR L2 OR L3
L4 12836 L1 OR L2 OR L3

=> s L4 and epoxide
L5 515 L4 AND EPOXIDE

=> s L5 AND (thiol OR mercaptan OR desulfurization)
L6 102 L5 AND (THIOL OR MERCAPTAN OR DESULFURIZATION)

=> s L6 AND (isopropanol OR butanediol OR (tetramethylene (w) glycol) OR
(dipropylene adj glycol))
L7 60 L6 AND (ISOPROPANOL OR BUTANEDIOL OR (TETRAMETHYLENE (W)
GLYCOL
) OR (DIPROPYLENE ADJ GLYCOL))

=> d L7 1-60 ti

L7 ANSWER 1 OF 60 USPATFULL on STN
TI CEMENT PRODUCTS AND METHODS OF MAKING AND USING THE SAME

L7 ANSWER 2 OF 60 USPATFULL on STN
TI Bioabsorbable Surgical Composition

L7 ANSWER 3 OF 60 USPATFULL on STN
TI Methods and Systems for Making ***Thiol*** Compounds from
Terminal
Olefinic Compounds

L7 ANSWER 4 OF 60 USPATFULL on STN

TI CURABLE COMPOSITIONS BASED ON POLYURETIDIONES, POLYTHIOLS AND
 PHOTOACTIVABLE BASES AND GENERATION OF ISOCYANATES FROM
 URETIDIONES

L7 ANSWER 5 OF 60 USPATFULL on STN
 TI Liquid fluorine-containing and two-component compositions for the
 surface treatment of mineral and non-mineral substrates

L7 ANSWER 6 OF 60 USPATFULL on STN
 TI ANTI-MICROBIAL AGENTS AND USES THEREOF

L7 ANSWER 7 OF 60 USPATFULL on STN
 TI Methods and compounds for curing polythiourethane compositions

L7 ANSWER 8 OF 60 USPATFULL on STN
 TI Methods and systems for the selective formation of thiourethane
 bonds
 and compounds formed therefrom

L7 ANSWER 9 OF 60 USPATFULL on STN
 TI ORGANOMETALLIC COMPOSITIONS AND COATING COMPOSITIONS

L7 ANSWER 10 OF 60 USPATFULL on STN
 TI Thiourethane Compositions and Processes for Making and Using Same

L7 ANSWER 11 OF 60 USPATFULL on STN
 TI Method of producing flexible laminates

L7 ANSWER 12 OF 60 USPATFULL on STN
 TI Hardener for Epoxy Resin and Epoxy Resin Composition

L7 ANSWER 13 OF 60 USPATFULL on STN
 TI MICROBIAL TRANSFORMATION METHOD FOR THE PREPARATION OF AN
 EPOTHILONE

L7 ANSWER 14 OF 60 USPATFULL on STN
 TI ***MERCAPTAN*** -HARDENED EPOXY POLYMER COMPOSITIONS AND
 PROCESSES
 FOR MAKING AND USING SAME

L7 ANSWER 15 OF 60 USPATFULL on STN
 TI POLYMER COMPOSITIONS AND PROCESSES FOR MAKING AND USING SAME

L7 ANSWER 16 OF 60 USPATFULL on STN
 TI Copper-catalyzed formation of carbon-heteroatom and carbon-carbon
 bonds

L7 ANSWER 17 OF 60 USPATFULL on STN
 TI ORGANOMETALLIC COMPOSITIONS AND COATING COMPOSITIONS

L7 ANSWER 18 OF 60 USPATFULL on STN
 TI Pyrrolotriazine inhibitors of kinases

L7 ANSWER 19 OF 60 USPATFULL on STN
 TI Polythiourethane compositions and processes for making and using
 same

L7 ANSWER 20 OF 60 USPATFULL on STN
 TI Retroviral protease inhibitors

L7 ANSWER 21 OF 60 USPATFULL on STN
TI Retroviral protease inhibitors

L7 ANSWER 22 OF 60 USPATFULL on STN
TI ***Thiol*** ester compositions and processes for making and
using
same

L7 ANSWER 23 OF 60 USPATFULL on STN
TI Organometallic compositions and coating compositions

L7 ANSWER 24 OF 60 USPATFULL on STN
TI Pyrrolotriazine inhibitors of kinases

L7 ANSWER 25 OF 60 USPATFULL on STN
TI Controlled release fertilizer material and process for production
thereof

L7 ANSWER 26 OF 60 USPATFULL on STN
TI Pyrrolotriazine inhibitors of kinases

L7 ANSWER 27 OF 60 USPATFULL on STN
TI Radiation-curable coatings for plastic substrates from
multifunctional
acrylate oligomers

L7 ANSWER 28 OF 60 USPATFULL on STN
TI Copper-catalyzed formation of carbon heteroatom and carbon-carbon
bonds

L7 ANSWER 29 OF 60 USPATFULL on STN
TI Anionic and Lewis base photopolymerization process and its use
for
making optical articles

L7 ANSWER 30 OF 60 USPATFULL on STN
TI ***Thiol*** ester compositions and processes for making and
using
same

L7 ANSWER 31 OF 60 USPATFULL on STN
TI ***Thiol*** ester compositions and processes for making and
using
same

L7 ANSWER 32 OF 60 USPATFULL on STN
TI Compositions useful as coatings, their preparation, and articles
made
therefrom

L7 ANSWER 33 OF 60 USPATFULL on STN
TI Anionic and Lewis base photopolymerization process and its use
for
making optical articles

L7 ANSWER 34 OF 60 USPATFULL on STN
TI Photocrosslinked hydrogel blend surface coatings

L7 ANSWER 35 OF 60 USPATFULL on STN
TI Dual cure reaction products of self-photoinitiating

multifunctional

acrylates with ***thiols*** and synethetic methods

L7 ANSWER 36 OF 60 USPATFULL on STN

TI Novel mono- and di-fluorinated beozothiepine copmunds as inhibitors of apical sodium co-dependent bile acid transport (ASBT) and taurocholate uptake

L7 ANSWER 37 OF 60 USPATFULL on STN

TI Microbial transformation method for the preparation of an epothilone

L7 ANSWER 38 OF 60 USPATFULL on STN

TI Microbial transformation method for the preparation of an epothilone

L7 ANSWER 39 OF 60 USPATFULL on STN

TI Novel mono- and di-fluorinated benzothiepine compounds as inhibitors of apical sodium co-dependent bile acid transport (ASBT) and taurocholate uptake

L7 ANSWER 40 OF 60 USPATFULL on STN

TI Dental polymer film

L7 ANSWER 41 OF 60 USPATFULL on STN

TI Copper-catalyzed formation of carbon-heteroatom and carbon-carbon bonds

L7 ANSWER 42 OF 60 USPATFULL on STN

TI Novel benzothiepinines having activity as inhibitors of lleal bile acid transport and taurocholate uptake

L7 ANSWER 43 OF 60 USPATFULL on STN

TI High strength epoxy adhesive and uses thereof

L7 ANSWER 44 OF 60 USPATFULL on STN

TI Copper-catalyzed formation of carbon-heteroatom and carbon-carbon bonds

L7 ANSWER 45 OF 60 USPATFULL on STN

TI Retroviral protease inhibitors

L7 ANSWER 46 OF 60 USPATFULL on STN

TI Composition of epoxy resin, chain extender and polymeric toughener with separate base catalyst

L7 ANSWER 47 OF 60 USPATFULL on STN

TI Substituted 5-aryl-benzothiepinines having activity as inhibitors of ileal bile acid transport and taurocholate uptake

L7 ANSWER 48 OF 60 USPATFULL on STN

TI Primerless substrate repair with polyepoxide and polythiol

L7 ANSWER 49 OF 60 USPATFULL on STN
TI Reacting methylene and alkene components in presence of tertiary amine
reacted with ***epoxide***

L7 ANSWER 50 OF 60 USPATFULL on STN
TI Isocyanate reactive blends and internal mould release composites

L7 ANSWER 51 OF 60 USPATFULL on STN
TI Isocyanate reactive blends and internal mould release compositions

L7 ANSWER 52 OF 60 USPATFULL on STN
TI Thermally curable mixture containing epoxy and formamide compounds

L7 ANSWER 53 OF 60 USPATFULL on STN
TI Isocyanate reactive blends and internal mould release compositions

L7 ANSWER 54 OF 60 USPATFULL on STN
TI Reaction product of olefinically unsaturated compounds with compounds
containing active hydrogen, processes for their preparation and 2-component lacquers based thereon

L7 ANSWER 55 OF 60 USPATFULL on STN
TI Reaction product of olefinically unsaturated compounds with compounds
containing active hydrogen, processes for their preparation and 2-component lacquers based thereon HOE 85/F 036J

L7 ANSWER 56 OF 60 USPATFULL on STN
TI Epoxy/nucleophile transesterification catalysts and thermoset coatings

L7 ANSWER 57 OF 60 USPATFULL on STN
TI Heat-hardenable ***epoxide*** resin mixtures

L7 ANSWER 58 OF 60 USPATFULL on STN
TI Process for the preparation of polyamines from N-monoaryl-N',N'-dialkyl urea compounds and their use for the synthesis of polyurethanes

L7 ANSWER 59 OF 60 USPATFULL on STN
TI Process for the preparation of stabilized polymer dispersions in polyol
at low temperature

L7 ANSWER 60 OF 60 USPATFULL on STN
TI Polyepoxide curing by polymercaptans catalyzed by dimethylamino alkyl ethers

=> d L7 30,31,49 ibib hit

L7 ANSWER 30 OF 60 USPATFULL on STN
ACCESSION NUMBER: 2005:227539 USPATFULL <<LOGINID::20091205>>
TITLE: ***Thiol*** ester compositions and processes

for

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	NUMBER	KIND	DATE
PATENT INFORMATION:	US 20050197391	A1	20050908
APPLICATION INFO.:	US 2005-60675	A1	20050217 (11)

	NUMBER	DATE
PRIORITY INFORMATION:	US 2004-545260P	20040217 (60)
	US 2004-561614P	20040413 (60)
	US 2004-561685P	20040413 (60)
	US 2004-561855P	20040413 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION
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NUMBER OF CLAIMS: 32
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 14 Drawing Page(s)
LINE COUNT: 6332

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI ***Thiol*** ester compositions and processes for making and
using

same
AB ***Thiol*** ester compositions, methods of making the
thiol
ester compositions, and methods of using the ***thiol***
ester
compositions are provided. In some embodiments, the ***thiol***
ester compositions include ***thiol*** esters, hydroxy
thiol
esters and cross-linked ***thiol*** esters. The ***thiol***
ester composition can be used to produce cross-linked
thiol
esters, sulfonic acid-containing esters, sulfonate containing
esters and
thioacrylate containing esters. The ***thiol*** ester
compositions
can be used to produce polythiourethanes. The polythiourethanes
can be
used in fertilizers and fertilizer coatings.

SUMM The invention relates to ***thiol*** containing ester
compositions
generally made from a reaction of unsaturated ester compositions

and a material capable of forming a ***thiol*** group. The invention also relates to the processes for preparing such ***thiol*** containing compositions and uses for the ***thiol*** containing compositions.

SUMM The present invention advantageously provides ***thiol*** containing compositions and methods of making such compositions.

In addition to the compositions and methods of making such compositions, products that include such compositions are also provided.

SUMM As an embodiment of the present invention, a ***thiol*** ester composition is advantageously provided. In this embodiment, the ***thiol*** ester composition includes ***thiol*** ester molecules that have an average of at least 1.5 ester groups per ***thiol*** ester molecule. The ***thiol*** ester molecules also have an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule. The ***thiol*** ester molecules also have a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

SUMM In some aspects, the ***thiol*** ester molecules have a molar ratio of cyclic sulfides to ***thiol*** groups ranging from 0 to 1.0. In some aspects, the ***thiol*** ester molecules have an average ranging from 1.5 to 9 ***thiol*** groups per ***thiol*** ester molecule. In some embodiments, the ***thiol*** ester molecules have a molar ratio of carbon-carbon double bonds to ***thiol*** groups of less than 1.5.

SUMM The amount of ***thiol*** sulfur or ***mercaptan*** sulfur contained within the ***thiol*** ester molecules can also vary. For example, in some embodiments, the ***thiol*** ester molecules have an average of greater than 5 weight percent ***thiol*** sulfur. In other embodiments, the ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur. In some embodiments, the ***thiol*** ester molecules have an average of less than 30 mole percent sulfur, which is present as cyclic sulfides. Alternatively, the ***thiol*** ester molecules have an average of less than 2 mole percent sulfur present as cyclic sulfides.

SUMM In some embodiments, the ***thiol*** ester molecules are produced from unsaturated esters that have an average of less than 25 weight percent of side chains that include 3 contiguous methylene interrupted carbon-carbon double bonds. In another aspect, greater than 40 percent of the total side chains contained within the ***thiol*** ester molecules contain sulfur.

SUMM In addition to the ***thiol*** ester composition, a process for producing the ***thiol*** ester composition is advantageously provided as another embodiment of the present invention. To produce the ***thiol*** ester composition, hydrogen sulfide is contacted with an unsaturated ester composition. The unsaturated ester composition includes unsaturated esters that have an average of at least 1.5 ester groups per unsaturated ester molecule. The unsaturated esters also have an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are reacted to produce or form the ***thiol*** ester composition. The ***thiol*** ester composition advantageously includes ***thiol*** ester molecules that have a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

SUMM Another process for producing the ***thiol*** ester composition is advantageously provided as another embodiment of the present invention. In this process embodiment, the hydrogen sulfide and the unsaturated ester composition are contacted. The unsaturated ester composition includes unsaturated esters having an average of at least 1.5 ester groups per unsaturated ester molecule and having an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are then reacted in a substantial absence of a solvent to form the ***thiol*** ester composition. The ***thiol*** ester composition includes ***thiol*** ester molecules. The ***thiol*** ester composition advantageously includes ***thiol*** ester molecules that have a molar ratio of cyclic sulfides to ***thiol*** groups of less than

1.5.

SUMM The resulting ***thiol*** ester molecules produced by this process possess advantageous characteristics. For example, in some embodiments, the ***thiol*** ester molecules have a molar ratio of the hydrogen sulfide to carbon-carbon double bonds of greater than 2. As another example, in other embodiments, the ***thiol*** ester molecules have an average of greater than 5 weight percent ***thiol*** sulfur. In some aspects, greater than 40 percent of the ***thiol*** ester molecule total side chains contain sulfur.

SUMM As another embodiment of the present invention, another process for preparing the ***thiol*** ester composition is advantageously provided. In this embodiment, a polyol composition and a thiolcarboxylic acid composition are contacted and reacted to produce the ***thiol*** ester composition. The ***thiol*** ester composition includes ***thiol*** ester molecules having an average of at least 1.5 ester groups per ***thiol*** ester molecule and having an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule.

SUMM In addition to the ***thiol*** ester composition, other compositions are advantageously provided as embodiments of the present invention. For example, a hydroxy ***thiol*** ester composition is provided as another embodiment of the present invention. The hydroxyl ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules having an average of at least 1.5 ester groups per hydroxy ***thiol*** ester molecule and having an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

SUMM As described herein, the .alpha.-hydroxy ***thiol*** groups contain an alcohol or hydroxy group and a ***thiol*** group within the same group. In embodiments of the present invention, the .alpha.-hydroxy ***thiol*** groups can be replaced with separate alcohol and ***thiol*** groups. In these embodiments, the same number of .alpha.-hydroxy groups can be used for the separate alcohol and ***thiol*** groups. For example, in some embodiments, the

hydroxy ***thiol*** ester molecules have an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups. In embodiments that contain separate alcohol and ***thiol*** groups, the hydroxy ***thiol*** ester molecules would contain an average of at least 1.5 alcohol groups and an average of at least 1.5 ***thiol*** groups.

SUMM In some aspects, the hydroxy ***thiol*** ester molecules have an average ranging from 1.5 to 9 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule. In some embodiments, the ***thiol*** ester molecules have a molar ratio of carbon-carbon double bonds to ***thiol*** groups of less than 1.5.

SUMM In some embodiments, the ***thiol*** ester molecules are produced from unsaturated esters that have an average of less than 25 weight percent of side chains that include 3 contiguous methylene interrupted carbon-carbon double bonds. In another aspect, greater than 40 percent of the total side chains contained within the .alpha.-hydroxy ***thiol*** ester molecules contain sulfur.

SUMM The amount of ***thiol*** sulfur contained within the hydroxy ***thiol*** ester molecules can also vary. For example, in some embodiments, the hydroxy ***thiol*** ester molecules have an average of greater than 5 weight percent ***thiol*** sulfur. In other embodiments, the hydroxy ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur.

SUMM In some embodiments, the hydroxy ***thiol*** ester molecules have a molar ratio of ***epoxide*** groups to the .alpha.-hydroxy ***thiol*** groups of less than 2. In other aspects, the composition is substantially free of ***epoxide*** groups.

SUMM In addition to the hydroxy ***thiol*** ester composition, methods or processes for making the hydroxy ***thiol*** ester composition are advantageously provided as embodiments of the present invention. In an embodiment, a process for preparing the hydroxy ***thiol*** ester composition is provided that includes the step of contacting the hydrogen sulfide and an epoxidized unsaturated ester composition. The epoxidized unsaturated ester composition includes epoxidized

unsaturated
esters having an average of at least 1.5 ester groups per
epoxidized
unsaturated ester molecule and having an average of at least 1.5
epoxide groups per epoxidized unsaturated ester
molecule. The
hydrogen sulfide and the epoxidized unsaturated esters are then
reacted
to form the hydroxy ***thiol*** ester composition.

SUMM In some embodiments, a molar ratio of the hydrogen sulfide to
epoxide groups in the epoxidized unsaturated esters is
greater
than 1.

SUMM Another process for preparing the hydroxy ***thiol*** ester
composition is advantageously provided as another embodiment of
the
present invention. In this process embodiment, a polyol
composition and
a hydroxy ***thiol*** carboxylic acid composition are
contacted and
reacted to produce the hydroxy ***thiol*** ester composition.
In
this embodiment, the hydroxy ***thiol*** ester composition
includes
hydroxy ***thiol*** ester molecules having an average of at
least
1.5 ester groups per hydroxy ***thiol*** ester molecule and
having
an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups
per
hydroxy ***thiol*** ester molecule.

SUMM A cross-linked ***thiol*** ester composition is
advantageously
provided as another embodiment of the present invention. The
cross-linked ***thiol*** ester composition includes
thiol
ester oligomers having at least two ***thiol*** ester
monomers
connected by a polysulfide linkage having a structure -S.sub.Q-,
wherein
Q is greater than 1. In some embodiments, the ***thiol***
ester
oligomers have at least three ***thiol*** ester monomers
connected
by polysulfide linkages. In another aspect, the ***thiol***
ester
oligomers have from 3 to 20 ***thiol*** ester monomers
connected by
polysulfide linkages.

SUMM In an aspect, the cross-linked ***thiol*** ester composition
includes both ***thiol*** ester monomers and ***thiol***
ester
oligomers. In some embodiments, the ***thiol*** ester
monomers and
thiol ester oligomers have a total ***thiol***
sulfur

content ranging from 0.5 to 8 weight percent; or alternatively, ranging from 8 to 15 weight percent. The combined ***thiol*** ester monomers and ***thiol*** ester oligomers can have an average molecular weight greater than 2000; or alternatively, in a range from 2000 to 20,000.

SUMM As another embodiment of the present invention, a cross-linked ***thiol*** ester composition produced by the process comprising the steps of contacting the ***thiol*** ester composition with an oxidizing agent and reacting the ***thiol*** ester and the oxidizing agent to form ***thiol*** ester oligomers is advantageously provided. In this embodiment, the ***thiol*** ester oligomers have at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure $-S_{\text{sub.Q-}}$, wherein Q is greater than 1.

SUMM A process to produce the cross-linked ***thiol*** ester composition is also advantageously provided as another embodiment of the present invention. In this process, a ***thiol*** ester composition is contacted and reacted with an oxidizing agent to form ***thiol*** ester oligomers having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure $-S_{\text{sub.Q-}}$, wherein Q is greater than 1. In some embodiments, the oxidizing agent is elemental sulfur, oxygen, or hydrogen peroxide. In an aspect, the oxidizing agent is elemental sulfur.

SUMM In an aspect, the ***thiol*** ester is a hydroxy ***thiol*** ester. In other aspects, a weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester molecules ranges from 0.5 to 32.

SUMM The step of the reacting the ***thiol*** ester and the oxidizing agent can be performed at a temperature ranging from 25.degree. C. to 150.degree. C. The process for producing the cross-linked ***thiol*** ester composition can also include the step of stripping residual hydrogen sulfide from the cross-linked ***thiol*** ester composition produced. In another aspect, the reaction of the ***thiol*** ester and the elemental sulfur is catalyzed. In some embodiments, the catalyst is an amine.

SUMM In another of its aspects, the present invention relates to a controlled release fertilizer material comprising a particulate plant nutrient surrounded by a coating which is the reaction product of a mixture comprising: (i) a first component selected from an isocyanate and/or an epoxy resin, and (ii) a first active hydrogen-containing compound selected from the group consisting of: a ***thiol*** ester composition; a hydroxy ***thiol*** ester composition; a cross-linked ***thiol*** ester composition and mixtures thereof.

SUMM In another of its aspects, the present invention relates to a process for the production of abrasion resistant polythiourethane and/or epoxy polymer encapsulated controlled release fertilizer particles by incorporating in urethane and/or epoxy polymer forming reaction mixture a sulfur-containing compound such as one or more of a ***thiol*** ester composition; a hydroxy ***thiol*** ester composition; a cross-linked ***thiol*** ester composition, other sulfur-based compounds described herein below and mixtures thereof.

SUMM Preferably, for the production of the present polythiourethane encapsulated controlled release fertilizer material, a sulfur-containing compound (e.g., one or more of a ***thiol*** ester composition; a hydroxy ***thiol*** ester composition; a cross-linked ***thiol*** ester composition) is used as one of the isocyanate-reactive components (alone or in combination with other active hydrogen-containing compounds). Preferably, the sulfur-containing compound comprises a sulfur-containing vegetable oil. In one preferred embodiment, the sulfur-containing vegetable oil comprises a mercaptanized vegetable oil (MVO), more preferably as described in more detail herein, even more preferably an MVO produced by the addition of hydrogen sulfide to a vegetable oil. In another preferred embodiment, the sulfur-containing vegetable oil comprises mercapto-hydroxy vegetable oil (MHVO), more preferably as described in more detail herein, even more preferably an MHVO produced by the addition of hydrogen sulfide to epoxidized vegetable oil. In yet another preferred embodiment, the sulfur-containing vegetable oil comprises sulfur cross-linked mercaptanized vegetable oil (CMVO), more preferably as described in more detail

herein, even more preferably an CMVO produced by the addition of elemental sulfur to mercaptanized vegetable oil (MVO).

SUMM Preferably, for the production of epoxy polymer encapsulated controlled release fertilizer material, a sulfur-containing compound (e.g., one or more of a ***thiol*** ester composition; a hydroxy ***thiol*** ester composition; a cross-linked ***thiol*** ester composition) is used as one of the isocyanate-reactive components (alone or in combination with other active hydrogen-containing compounds). Preferably, the sulfur-containing compound comprises a sulfur-containing vegetable oil (e.g., MVO and/or MHVO and/or CMVO) is used as one of the epoxy resin-reactive components.

DRWD FIG. 1 includes two graphs that compare the NMR's of soybean oil, which is shown in the top graph, and a ***thiol*** containing ester produced from soybean oil in accordance with an embodiment of the present invention, which is shown in the bottom graph;

DRWD FIG. 2 includes two graphs that compare the NMR's of epoxidized soybean oil, which is shown in the top graph, and a ***thiol*** containing ester produced from epoxidized soybean oil in accordance with an embodiment of the present invention, which is shown in the bottom graph;

DRWD FIG. 3 is a gas chromatograph (GC)/mass spectrometer (MS) trace of a ***thiol*** containing ester that was produced from soybean oil in accordance with an embodiment of the present invention and then treated by methanolysis;

DRWD FIG. 5 is a GC/MS trace of hydroxy ***thiol*** containing ester produced from epoxidized soybean oil in accordance with an embodiment of the present invention and then treated by methanolysis;

DETD In this specification, " ***thiol*** ester composition" refers to an ester composition that includes " ***thiol*** ester molecules." The

thiol ester molecule has at least one ***thiol*** group and at least one ester group within the ***thiol*** ester molecule.

DETD In this specification, "hydroxy ***thiol*** ester composition"

refers to an ester composition that includes "hydroxy ***thiol*** ester molecules." The hydroxy ***thiol*** ester molecule has at least one ***thiol*** group, at least one ester group, and at least one hydroxy or alcohol group within the hydroxy ***thiol***

ester molecule. Alternatively, the alcohol group and the ***thiol*** group can be combined in the same group, which is referred to as an ".alpha.-hydroxy ***thiol*** group."

DETD In this specification, "polythiourethane" refers to a urethane composition that includes more than one of the following structure:

##STR1## The presence of the thiourethane group can be determined by method known to those skilled in the art (for example infrared spectroscopy, Raman spectroscopy, and/or NMR). ***Thiol***

Ester Composition

DETD The present invention advantageously provides a ***thiol*** ester composition as an embodiment of the present invention. The ***thiol*** ester composition includes ***thiol*** ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule. The ***thiol*** ester composition also has a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5, as described herein.

DETD Generally, the ***thiol*** ester composition contains molecules having at least one ester group and at least one ***thiol*** group. The ***thiol*** ester composition of this invention can be produced from any unsaturated ester, as described herein. Because the feedstock unsaturated esters can contain multiple carbon-carbon double bonds per unsaturated ester molecule, carbon-carbon double bond reactivity and statistical probability dictate that each ***thiol*** ester molecule of the ***thiol*** ester composition produced from the unsaturated ester composition will not have the same number of ***thiol*** groups, number of unreacted carbon-carbon double bonds, number of cyclic sulfides, molar ratio of carbon-carbon double bonds to ***thiol*** groups, molar ratio of cyclic sulfides to ***thiol*** groups and other quantities of functional groups and molar ratios disclosed herein as the feedstock unsaturated ester. Additionally, the feedstock unsaturated esters can also comprise a mixture of individual unsaturated esters having a different number of carbon-carbon double bonds and/or ester groups. Thus, many of these properties will be discussed as an average number of the groups per ***thiol*** ester molecule

within the ***thiol*** ester composition or average ratio per ***thiol*** ester molecule within the ***thiol*** ester composition. In other embodiments, it is desired to control the content of ***thiol*** sulfur present in the ***thiol*** ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every carbon-carbon double bond within the unsaturated ester, certain molecules of ***thiol*** ester can have more or less ***thiol*** groups than other molecules. Thus, the weight percent of ***thiol*** groups is stated as an average across all ***thiol*** ester molecules of the ***thiol*** ester composition.

DETD The ***thiol*** ester can be derived from any unsaturated ester described herein.

DETD The ***thiol*** ester compositions can be described as comprising one or more separate or discreet functional groups of the ***thiol*** ester molecule and/or ***thiol*** ester composition. These independent functional groups can include: the number of (or average number of) ester groups per ***thiol*** ester molecule, ***thiol*** containing the number of (or average number of) ***thiol*** groups per ***thiol*** ester molecule, the number of (or average number of) unreacted carbon-carbon double bonds per ***thiol*** ester molecule, the average ***thiol*** sulfur content of the ***thiol*** ester composition, the percentage (or average percentage) of sulfide linkages per ***thiol*** ester molecule, and the percentage (or average percentage) of cyclic sulfide groups per ***thiol*** ester molecule. Additionally, the ***thiol*** ester compositions can be described using individual or a combination of ratios including the ratio of double bonds to ***thiol*** groups, the ratio of cyclic sulfides to ***mercaptan*** group, and the like.

As separate elements, these functional groups of the ***thiol*** composition will be described separately.

DETD Minimally, in some embodiments, the ***thiol*** ester contains ***thiol*** ester molecules having at least one ester group and one ***thiol*** group per ***thiol*** ester molecule. As the ***thiol*** ester is prepared from unsaturated esters, the

thiol ester can contain the same number of ester groups as the unsaturated esters described herein. In an embodiment, the ***thiol*** ester molecules have an average of at least 1.5 ester groups per ***thiol*** ester molecule. Alternatively, the ***thiol*** ester molecules have an average of at least 2 ester groups per ***thiol*** ester molecule, alternatively, an average of at least 2.5 ester groups per ***thiol*** ester molecule; or alternatively, an average of at least 3 ester groups per ***thiol*** ester molecule. In other embodiments, the ***thiol*** esters have an average of from 1.5 to 8 ester groups per ***thiol*** ester molecule; alternatively, an average of from 2 to 7 ester groups per ***thiol*** ester molecule; alternatively, an average of from 2.5 to 5 ester groups per ***thiol*** ester molecule; or alternatively, an average of from 3 to 4 ester groups per ***thiol*** ester molecule. In yet other embodiments, the ***thiol*** ester comprises an average of 3 ester groups per ***thiol*** ester molecule or alternatively, an average of 4 ester groups per unsaturated ester molecule.

DETD Minimally, the ***thiol*** ester comprises an average of at least one ***thiol*** group per ***thiol*** ester molecule. In an embodiment, the ***thiol*** ester molecules have an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule; alternatively, ***thiol*** containing an average of at least 2 ***thiol*** groups per ***thiol*** ester molecule; alternatively, an average of at least 2.5 ***thiol*** groups per ***thiol*** ester molecule; or alternatively, an average of at least 3 ***thiol*** groups per ***thiol*** ester molecule. In other embodiments, the ***thiol*** ester molecules have an average of from 1.5 to 9 ***thiol*** groups per ***thiol*** ester molecule; alternatively, an average of from 3 to 8 ***thiol*** groups per ***thiol*** ester molecule; alternatively, ***thiol*** containing an average of from 2 to 4 ***thiol*** groups per ***thiol*** ester molecule, or alternatively, an average of from 4 to 8 ***thiol*** groups per ***thiol*** ester molecule.

DETD In other embodiments, the ***thiol*** ester can be described

by the average amount of ***thiol*** sulfur present in ***thiol*** ester. In an embodiment, the ***thiol*** ester molecules have an average of at least 5 weight percent ***thiol*** sulfur per ***thiol*** ester molecule; alternatively, an average of at least 10 weight percent ***thiol*** sulfur per ***thiol*** ester molecule, or alternatively, an average of greater than 15 weight percent ***thiol*** sulfur per ***thiol*** ester molecule. In an embodiment, the ***thiol*** ester molecules have an average of from 5 to 25 weight percent ***thiol*** sulfur per ***thiol*** ester molecule; alternatively, an average of from 5 to 20 weight percent ***thiol*** sulfur per ***thiol*** ester molecule; alternatively, an average of from 6 to 15 weight percent ***thiol*** sulfur per ***thiol*** ester molecule; or alternatively, an average of from 8 to 10 weight percent ***thiol*** sulfur per ***thiol*** ester molecule.

DETD Generally, the location of the ***thiol*** group of the ***thiol*** ester is not particularly important and will be dictated by the method used to produce the ***thiol*** ester. In embodiments wherein the ***thiol*** ester is produced by contacting an unsaturated ester, the position of the ***thiol*** group will be dictated by the position of the carbon-carbon double bond. When the carbon-carbon double bond is an internal carbon-carbon double bond, the method of producing the ***thiol*** ester will result in a secondary ***thiol*** group. However, when the double bond is located at a terminal position it is possible to choose reaction conditions to produce a ***thiol*** ester comprising either a primary ***thiol*** group or a secondary ***thiol*** group.

DETD Some methods of producing the ***thiol*** ester composition can additionally create sulfur containing functional groups other than a ***thiol*** group. For example, in some ***thiol*** ester production methods, an introduced ***thiol*** group can react with a carbon-carbon double bond within the same unsaturated ester to produce a sulfide linkage. When the reaction is with a double bond of a second unsaturated ester, this produces a simple sulfide linkage. However, in some instances, the second carbon-carbon double bond is located in the

same unsaturated ester molecule. When the ***thiol*** group reacts with a second carbon-carbon double bond within the same unsaturated ester molecule, a sulfide linkage is produced. In some instances, the carbon-carbon double bond can be within a second ester group of the unsaturated ester molecule. While in other instances, the carbon-carbon double bond can be within the same ester group of the unsaturated ester molecule.

DETD When the ***thiol*** group reacts with the carbon-carbon double bond in a second ester group of the same unsaturated ester molecule, the cyclic sulfide would contain two ester groups contained within a ring structure. When the ***thiol*** group reacts with the carbon-carbon double bond within the same ester group, the cyclic sulfide would not contain an ester group within the ring structure. Within this specification, this second type of cyclic sulfide is referred to as a cyclic sulfide. Within this specification, the first type of cyclic sulfide is referred to as a simple sulfide. In the cyclic sulfide case, the sulfide linkage produces a cyclic sulfide functionality within a single ester group of the ***thiol*** ester. This linkage is termed a cyclic sulfide for purposes of this application. One such sulfide group that can be produced is a cyclic sulfide. The cyclic sulfide rings that can be produced include a tetrahydrothiopyran ring, a thietane ring, or a thiophane ring (tetrahydrothiophene ring).

DETD In some embodiments, it is desirable to control the average amount of sulfur present as cyclic sulfide in the ***thiol*** ester. In an embodiment the average amount of sulfur present as cyclic sulfide in the ***thiol*** ester molecules comprises less than 30 mole percent.

Alternatively, the average amount of sulfur present as cyclic sulfide in the ***thiol*** esters comprises less than 20 mole percent; alternatively, less than 10 mole percent; alternatively, less than 5 mole percent; or alternatively, less than 2 mole percent. In other embodiments, it is desired to control the molar ratio of cyclic sulfides to ***thiol*** groups. In other embodiments, it is desirable to have

molar ratios of cyclic sulfide to ***thiol*** group. In an embodiment, the average molar ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester is less than 1.5. Alternatively, the average molar ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester is less than 1; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, 0.1. In some embodiments, the ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester ranges from 0 to 1; or alternatively, the average molar ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester ranges between 0.05 and 1.

DETD In some instances it can be desirable to have carbon-carbon double bonds present in the ***thiol*** ester composition while in other embodiments it can be desirable to minimize the number of carbon-carbon double bonds present in the ***thiol*** ester composition.

The presence of carbon-carbon double bonds present in the ***thiol*** ester can be stated as an average molar ratio of carbon-carbon double bonds to ***thiol*** -sulfur. In an embodiment, the average ratio of the remaining unreacted carbon-carbon double bond in the ***thiol*** ester composition to ***thiol*** sulfur is less than 1.5 per ***thiol*** ester molecule. Alternatively, the average ratio of carbon-carbon double bond to ***thiol*** sulfur is less than 1.2 per ***thiol*** ester molecule; alternatively, less than 1.0 per ***thiol*** ester molecule; alternatively, less than 0.75 per ***thiol*** ester molecule; alternatively, less than 0.5 per ***thiol*** ester molecule; alternatively, less than 0.2 per ***thiol*** ester molecule; or alternatively, less than 0.1 per ***thiol*** ester molecule.

DETD In particular embodiments, the ***thiol*** ester is produced from unsaturated ester compositions. Because the feedstock unsaturated ester has particular compositions having a certain number of ester groups present, the product ***thiol*** ester composition will have about the same number of ester groups per ***thiol*** ester molecule as the feedstock unsaturated ester. Other, independent ***thiol*** ester properties described herein can be used to further describe the ***thiol*** ester composition.

DETD In some embodiments, the ***thiol*** ester molecules are produced from unsaturated esters having an average of less than 25 weight

percent of side chains having 3 contiguous methylene interrupted carbon-carbon double bonds, as described herein. In some embodiments, greater than 40 percent of the ***thiol*** containing natural source total side chains can include sulfur. In some embodiments, greater than 60 percent of the ***thiol*** ester molecule total side chains can include sulfur. In other embodiments, greater than 50, 70, or 80 percent of the ***thiol*** ester molecule total side chains can include sulfur.

DETD In an embodiment, the ***thiol*** ester is a ***thiol*** containing natural source oil, as described herein. When the ***thiol*** ester is a ***thiol*** containing natural source oil, functional groups that are present in the ***thiol*** containing natural source oil can be described in a "per ***thiol*** ester molecule" basis or in a "per triglyceride" basis. The ***thiol*** containing natural source oil can have substantially the same properties as the ***thiol*** ester composition, such as the molar ratios and other independent descriptive elements described herein.

DETD The average number of ***thiol*** groups per triglyceride in the ***thiol*** containing natural source oil is greater than about 1.5.

In some embodiments, the average number of ***thiol*** groups per triglyceride can range from about 1.5 to about 9.

DETD The ***thiol*** ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an unsaturated ester composition and can be further limited by the process as described herein. The ***thiol*** containing natural source oil can also be described using a molecular weight or an average molecular weight of the side chains.

DETD Hydroxy ***Thiol*** Ester Composition

DETD In embodiments of the present invention, the ***thiol*** ester compositions can also contain a hydroxy or alcohol group. When the ***thiol*** ester composition includes the hydroxy group, the ***thiol*** ester composition is referred to herein as the hydroxy ***thiol*** ester composition. The quantity or number of alcohol groups present in the hydroxy ***thiol*** ester composition can be

independent of the quantity of other functional groups present in the hydroxy ***thiol*** ester composition (i.e. ***thiol*** groups, ester groups, sulfides, cyclic sulfides). Additionally, the weight percent of ***thiol*** sulfur and functional group ratios (i.e. molar ratio of cyclic sulfides to ***thiol*** groups, molar ratio of ***epoxide*** groups to ***thiol*** groups, molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups and other disclosed quantities of functional groups and their molar ratios to the ***thiol*** groups) are separate or discrete elements that can be used to describe the hydroxy ***thiol*** ester composition. The hydroxy ***thiol*** ester composition can be described using any combination of the hydroxy ***thiol*** ester composition separate functional groups or ratios described herein. DETD In an embodiment, the hydroxy ***thiol*** ester composition is produced by reacting hydrogen sulfide with an epoxidized unsaturated ester composition as described herein. Because the epoxidized unsaturated ester can contain multiple ***epoxide*** groups, ***epoxide*** group reactivity and statistical probability dictate that not all hydroxy ***thiol*** ester molecules of the hydroxy ***thiol*** ester composition will have the same number of hydroxy groups, ***thiol*** groups, .alpha.-hydroxy ***thiol*** groups, sulfides, cyclic sulfides, molar ratio of cyclic sulfides to ***thiol*** groups, molar ratio of ***epoxide*** groups to ***thiol*** groups, molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups, weight percent ***thiol*** sulfur and other disclosed quantities of functional groups and their molar ratios as the epoxidized unsaturated ester composition. Thus, many of these properties will be discussed as an average number or ratio per hydroxy ***thiol*** ester molecule. In other embodiments, it is desired to control the content of ***thiol*** sulfur present in the hydroxy ***thiol*** ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every ***epoxide*** group within

the epoxidized unsaturated ester, certain hydroxy ***thiol***
ester molecules can have more or less ***thiol*** groups than other
molecules within the hydroxy ***thiol*** ester composition.
Thus, the weight percent of ***thiol*** groups can be stated as an
average weight percent across all hydroxy ***thiol*** ester
molecules.
DETD As an embodiment of the present invention, the hydroxy
thiol ester composition includes hydroxy ***thiol*** ester
molecules that have an average of at least 1 ester groups and an average of at
least 1 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol***
ester molecule. As an embodiment of the present invention, the hydroxy
thiol ester composition includes hydroxy ***thiol***
ester molecules that have an average of at least 1.5 ester groups and
an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups
per hydroxy ***thiol*** ester molecule.
DETD Minimally, in some embodiments, the hydroxy ***thiol***
ester comprises at least one ester, at least one ***thiol*** group,
and at least one hydroxy group. Because the hydroxy ***thiol***
ester is prepared from epoxidized unsaturated esters, the hydroxy
thiol ester can contain the same number of ester groups as the
epoxidized unsaturated esters. In an embodiment, the hydroxy ***thiol***
ester molecules have an average of at least 1.5 ester groups per
hydroxy ***thiol*** ester molecule. Alternatively, the hydroxy
thiol ester molecules have an average of at least 2 ester groups per
hydroxy ***thiol*** ester molecule; alternatively, an average of at
least 2.5 ester groups per hydroxy ***thiol*** ester molecule; or
alternatively, an average of at least 3 ester groups per hydroxy
thiol ester molecule. In other embodiments, the hydroxy
thiol esters have an average of from 1.5 to 8 ester
groups per hydroxy ***thiol*** ester molecule; alternatively, an average
of from 2 to 7 ester groups per hydroxy ***thiol*** ester
molecule; alternatively, an average of from 2.5 to 5 ester groups per
hydroxy ***thiol*** ester molecule; or alternatively, an average of
from 3 to 4 ester groups per hydroxy ***thiol*** ester molecule. In yet
other

embodiments, the .alpha.-hydroxy ***thiol*** ester comprises an average of 3 ester groups per hydroxy ***thiol*** ester molecule or alternatively, an average of 4 ester groups per hydroxy ***thiol*** ester molecule.

DETD In some embodiments, the hydroxy group and the ***thiol*** group are combined in the same group, which produces the .alpha.-hydroxy ***thiol*** group. In other embodiments, the ***thiol*** group and the hydroxy or alcohol group are not in the same group. When this occurs, to produce the hydroxy ***thiol*** ester composition, the alcohol group is added independently of the ***thiol*** group. For example, as another embodiment of the present invention, the hydroxy ***thiol*** ester composition advantageously includes hydroxy ***thiol*** ester molecules. The hydroxy ***thiol*** ester molecules have an average of at least 1.5 ester groups, an average of at least 1.5 ***thiol*** groups, and an average of at least 1.5 alcohol groups per hydroxy ***thiol*** ester molecule.

DETD Minimally, in some embodiments, the hydroxy ***thiol*** ester comprises at least one ***thiol*** group per hydroxy ***thiol*** ester molecule. In an embodiment, the hydroxy ***thiol*** ester molecules have an average of at least 1.5 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2.5 ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of at least 3 ***thiol*** groups per hydroxy ***thiol*** ester molecule. In other embodiments, the hydroxy ***thiol*** ester molecules have an average of from 1.5 to 9 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2 to 4 ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 4 to 8 ***thiol*** groups per hydroxy ***thiol*** ester.

DETD Minimally, in some embodiments, the hydroxy ***thiol*** ester

composition comprises an average of at least 1 hydroxy or alcohol group per hydroxy ***thiol*** ester molecule. In some embodiments, the hydroxy ***thiol*** ester composition comprises an average of at least 1.5 hydroxy groups per hydroxy ***thiol*** ester molecule; alternatively, average of at least 2 hydroxy groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2.5 hydroxy groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of at least 3 hydroxy groups per ***thiol*** ester molecule. In other embodiments, the ***thiol*** ester composition comprises an average of from 1.5 to 9 hydroxy groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 3 to 8 hydroxy groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2 to 4 hydroxy groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 4 to 8 hydroxy groups per hydroxy ***thiol*** ester molecule.

DETD In yet other embodiments, the number of hydroxy groups can be stated as an average molar ratio of hydroxy group to ***thiol*** groups. Minimally, in some embodiments, the molar ratio of hydroxy groups to ***thiol*** groups is at least 0.25. In some embodiments, the molar ratio of hydroxy groups to ***thiol*** groups is at least 0.5; alternatively, at least 0.75; alternatively, at least 1.0; alternatively, at least 1.25; or alternatively, at least 1.5. In other embodiments, the molar ratio of hydroxy groups to ***thiol*** groups ranges from 0.25 to 2.0; alternatively, from 0.5 to 1.5; or alternatively, from 0.75 to 1.25.

DETD In embodiments where the hydroxy ***thiol*** esters are produced from an epoxidized unsaturated ester, the hydroxy ***thiol*** esters can be described as containing ester groups and .alpha.-hydroxy ***thiol*** groups. The number of ester groups and the number of .alpha.-hydroxy ***thiol*** groups are independent elements and as such the hydroxy ***thiol*** esters can be described as having any combination of ester groups and .alpha.-hydroxy ***thiol*** groups described herein. Minimally, the hydroxy ***thiol*** ester comprises an average of at least 1 .alpha.-hydroxy ***thiol*** group per

hydroxy ***thiol*** ester molecule. In some embodiments, the hydroxy ***thiol*** ester composition comprises an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of at least 3 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule. In other embodiments, the hydroxy ***thiol*** ester composition comprises an average of from 1.5 to 9 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 3 to 8 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2 to 4 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 4 to 8 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

DETD The hydroxy ***thiol*** esters can be produced by contacting an epoxidized ester derived from an unsaturated ester (i.e., unsaturated ester), as described herein. In some instances it can be desirable to have ***epoxide*** groups present in the hydroxy ***thiol*** ester composition. While in other embodiments, it can be desirable to minimize the number of epoxy groups present in the hydroxy ***thiol*** ester composition. Thus, the presence of residual ***epoxide*** groups can be another separate functional group used to describe the hydroxy ***thiol*** ester.

DETD The presence of ***epoxide*** groups in the hydroxy ***thiol*** ester can be independently described as an average number of ***epoxide*** groups per hydroxy ***thiol*** ester, a molar ratio of ***epoxide*** groups to ***thiol*** groups, a molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups, or any combination thereof. In some embodiments, the hydroxy ***thiol*** ester molecules comprise an average of less than 2 ***epoxide*** groups per hydroxy ***thiol*** ester molecule, i.e., the hydroxy ***thiol*** ester molecules have a molar ratio of

epoxide
 groups to .alpha.-hydroxy ***thiol*** groups of less than 2.
 Alternatively, the hydroxy ***thiol*** ester comprises an
 average of
 less than 1.5 ***epoxide*** groups per hydroxy ***thiol***
 ester
 molecule; alternatively, an average of less than 1
 epoxide
 group per hydroxy ***thiol*** ester molecule; alternatively,
 an
 average of less than 0.75 ***epoxide*** groups per hydroxy
 thiol ester molecule; or alternatively, an average of
 less than
 0.5 ***epoxide*** groups per hydroxy ***thiol*** ester
 molecule.
 In other embodiments, the molar ratio of ***epoxide*** groups
 to
 thiol groups averages less than 1.5. Alternatively, the
 molar
 ratio of ***epoxide*** groups to ***thiol*** groups
 averages
 less than 1; alternatively, averages less than 0.75;
 alternatively,
 averages less than 0.5; alternatively, averages less than 0.25;
 or
 alternatively, averages less than 0.1. In yet other embodiments,
 the
 molar ratio of ***epoxide*** groups to .alpha.-hydroxy
 thiol
 groups averages less than 1.5. Alternatively, the molar ratio of
 epoxide groups to .alpha.-hydroxy ***thiol***
 groups
 averages less than 1; alternatively, averages less than 0.75;
 alternatively, averages less than 0.5; alternatively, averages
 less than
 0.25; or alternatively, averages less than 0.1.
 DETD In some embodiments, the hydroxy ***thiol*** ester
 composition is
 substantially free of ***epoxide*** groups.
 DETD In other embodiments, the hydroxy ***thiol*** ester can be
 described by the average amount of ***thiol*** sulfur present
 in
 hydroxy ***thiol*** ester. In an embodiment, the hydroxy
 thiol ester molecules have an average of at least 2.5
 weight
 percent ***thiol*** sulfur per hydroxy ***thiol*** ester
 molecule; alternatively, an average of at least 5 weight percent
 thiol sulfur per hydroxy ***thiol*** ester
 molecule;
 alternatively, an average of at least 10 weight percent
 thiol
 sulfur per hydroxy ***thiol*** ester molecule; or
 alternatively, an
 average of greater than 15 weight percent ***thiol*** sulfur
 per
 hydroxy ***thiol*** ester molecule. In an embodiment, the
 hydroxy
 thiol ester molecules have an average of from 5 to 25
 weight
 percent ***thiol*** sulfur per hydroxy ***thiol*** ester

molecule; alternatively, an average of from 5 to 20 weight percent

thiol sulfur per hydroxy ***thiol*** ester molecule;

alternatively, an average of from 6 to 15 weight percent

thiol sulfur per hydroxy ***thiol*** ester molecule; or

alternatively, an average of from 8 to 10 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule.

DETD In some embodiments, at least 20 percent of the total side chains

include the .alpha.-hydroxy ***thiol*** group. In some embodiments,

at least 20 percent of the total side chains include the .alpha.-hydroxy

thiol group. In some embodiments, at least 60 percent of the

total side chains include the .alpha.-hydroxy ***thiol*** group;

alternatively, at least 70 percent of the total side chains include the

.alpha.-hydroxy ***thiol*** group. Yet in other embodiments, at

least 80 percent of the total side chains include the .alpha.-hydroxy

thiol group.

DETD In some aspects, greater than 20 percent of the hydroxy

thiol ester molecule total side chains contain sulfur. In some aspects,

greater than 40 percent of the hydroxy ***thiol*** ester molecule

total side chains contain sulfur. In some aspects, greater than

60 percent of the hydroxy ***thiol*** ester molecule total side chains

contain sulfur; alternatively, greater than 70 percent of the total side

chains contain sulfur; or alternatively, greater than 80 percent of the

total side chains contain sulfur.

DETD In particular embodiments, the epoxidized unsaturated ester used in the

synthesis of the hydroxy ***thiol*** ester is produced from the

epoxidized unsaturated ester composition that includes an epoxidized

natural source oil. Because the natural source oils have particular

compositions regarding the number of ester groups present, the hydroxy

thiol ester will have about the same number of ester groups as

the feedstock natural source oil. Other independent properties that are

described herein can be used to further describe the hydroxy

thiol ester.

DETD In other embodiments, the epoxidized unsaturated ester used to produce

the hydroxy ***thiol*** ester is produced from synthetic (or

semi-synthetic) unsaturated ester oils. Because the synthetic ester oils can have particular compositions regarding the number of ester groups present, the hydroxy ***thiol*** ester would have about the same number of ester groups as the synthetic ester oil. Other, independent properties of the unsaturated ester, whether the unsaturated ester includes natural source or synthetic oils, can be used to further describe the hydroxy ***thiol*** ester composition.

DETD The hydroxy ***thiol*** ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an epoxidized unsaturated ester composition and can be further limited by the process as described herein. The hydroxy ***thiol*** containing natural source oil can also be described using an average molecular weight or an average molecular weight of the side chains.

DETD Cross-Linked ***Thiol*** Ester Compositions

DETD In an aspect, the present invention relates to a cross-linked ***thiol*** ester composition. Generally, the cross-linked ***thiol*** ester molecules are oligomers of ***thiol*** esters that are connected together by polysulfide linkages -S.sub.x- wherein x is an integer greater 1. As the cross-linked ***thiol*** ester is described as an oligomer of ***thiol*** esters, the ***thiol*** esters can be described as the monomer from which the cross-linked ***thiol*** esters are produced.

DETD In an aspect, the cross-linked ***thiol*** ester composition comprises a ***thiol*** ester oligomer having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure -S.sub.Q-, wherein Q is an integer greater than 1. In an aspect, the polysulfide linkage may be the polysulfide linkage -S.sub.Q-, wherein Q is 2, 3, 4, or mixtures thereof. In other embodiments, Q can be 2; alternatively, 3; or alternatively, 4.

DETD In an aspect, the cross-linked ***thiol*** ester composition comprises a ***thiol*** ester oligomer having at least 3 ***thiol*** ester monomers connected by polysulfide linkages; alternatively, 5 ***thiol*** ester monomers connected by polysulfide linkages; alternatively, 7 ***thiol*** ester monomers connected by polysulfide linkages; or alternatively, 10 ***thiol*** ester monomers connected by polysulfide linkages. In yet other embodiments, the cross-linked ***thiol*** ester composition comprises a ***thiol*** ester oligomer having from 3 to 20 ***thiol*** ester

monomers connected by polysulfide linkages; alternatively, from 5 to 15

thiol ester monomers connected by polysulfide linkages; or

alternatively, from 7 to 12 ***thiol*** ester monomers connected by polysulfide linkages.

DETD In an aspect, the cross-linked ***thiol*** ester composition comprises ***thiol*** ester monomers and ***thiol***

oligomers. In some embodiments, the cross-linked ***thiol*** ester

composition has a combined ***thiol*** ester monomer and ***thiol*** ester oligomer average molecular weight greater than

2,000. In other embodiments, the cross-linked ***thiol*** ester

composition has a combined ***thiol*** ester monomer and ***thiol*** ester oligomer average molecular weight greater than

5,000; or alternatively, greater than 10,000. In yet other embodiments,

the cross-linked ***thiol*** ester composition has a combined ***thiol*** ester monomer and ***thiol*** ester oligomer

average molecular weight ranging from 2,000 to 20,000; alternatively, from 3,000

to 15,000; or alternatively, from 7,500 to 12,500.

DETD In an aspect, the ***thiol*** ester monomers and ***thiol***

ester oligomers have a total ***thiol*** sulfur content greater than

0.5. In other embodiments, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total ***thiol***

sulfur content greater than 1; alternatively, greater than 2; alternatively,

greater than 4. In yet other embodiments, the ***thiol*** ester

monomers and the ***thiol*** ester oligomers have a total ***thiol*** sulfur content from 0.5 to 8; alternatively, from

4 to 8; or alternatively, 0.5 to 4.

DETD In an aspect, the ***thiol*** ester monomers and ***thiol***

ester oligomers have a total sulfur content greater than 8. In some

embodiments, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total sulfur content greater than 10;

alternatively, greater than 12. In yet other embodiments, the ***thiol*** ester monomers and ***thiol*** ester

oligomers have a total sulfur content ranging from 8 to 15 weight percent; alternatively,

from 9 to 14; or alternatively, from 10 to 13.

DETD The cross-linked ***thiol*** ester compositions can also be described as a product produced by the process comprising

contacting a ***thiol*** ester with oxidizing agent and can be further

limited by

the process as described herein.

DETD The present invention advantageously includes sulfide-containing ester compositions as embodiments of the present invention. Generally, the sulfide-containing ester compositions can be described as containing molecules having at least one ester group and a least one sulfide group within each molecule. The sulfide-containing esters used in the present invention can be produced by contacting either an unsaturated ester or an epoxidized unsaturated ester with a ***thiol*** containing compound as described herein.

DETD The feedstock unsaturated esters can contain multiple carbon-carbon double bonds per unsaturated ester molecule. The carbon-carbon double bond reactivity and statistical probability, however, dictate that each sulfide-containing ester molecule of the ***thiol*** - containing ester composition produced from the unsaturated ester composition will not have the same number of sulfide groups, number of unreacted carbon-carbon double bonds, molar ratio of carbon-carbon double bonds to sulfide groups, molar ratio of cyclic sulfides to ***thiol*** groups and other herein disclosed quantities of functional groups and molar ratios. Additionally, the feedstock unsaturated esters can also comprise a mixture of individual unsaturated esters having a different number of carbon-carbon double bonds and/or ester groups. Many of these properties are discussed herein as an average number of the groups per sulfide-containing ester molecule within the sulfide-containing ester composition or average ratio per ***thiol*** -containing ester molecule within the sulfide-containing ester composition.

DETD In embodiments related to the sulfide-containing ester that is produced from an epoxidized unsaturated ester, the feedstock epoxidized unsaturated esters can contain multiple ***epoxide*** groups per unsaturated ester molecule. Individual ***epoxide*** group reactivity and statistical probability dictate that each sulfide-containing ester molecule of the sulfide-containing ester composition produced from the unsaturated ester composition will not have the same number of sulfide groups, number of unreacted ***epoxide*** groups, molar ratio of ***epoxide*** groups to sulfide groups, and other herein disclosed quantities of functional groups and molar ratios. Additionally, the feedstock epoxidized unsaturated esters can also comprise a mixture of individual

epoxidized
 unsaturated ester molecules having a different number of
 epoxide
 groups and/or ester groups. Thus, many of these properties are
 described
 as an average number of the groups per sulfide-containing ester
 molecules within the sulfide-containing ester composition or
 average
 ratio per ***thiol*** -containing ester molecule within the
 sulfide-containing ester composition.

DETD Minimally, in some embodiments, the sulfide-containing esters
 comprise
 at least one ester group per sulfide-containing ester molecule.
 In some
 embodiments, the sulfide-containing ester has an average of at
 least 1.5
 ester groups per sulfide-containing ester molecule.

Alternatively, the
 sulfide-containing ester molecules have an average of at least 2
 ester
 groups per sulfide-containing ester molecule; alternatively, an
 average
 of at least 2.5 ester groups per sulfide-containing ester
 molecule; or
 alternatively, an average of at least 3 ester groups per
 sulfide-containing ester molecule. In other embodiments, the
 sulfide-containing esters have an average of from 1.5 to 9 ester
 groups
 per sulfide-containing ester molecule; alternatively, an average
 of from
 1.5 to 8 ester groups per sulfide-containing ester molecule;
 alternatively, an average of from 2 to 8 ester groups per
 sulfide-containing ester molecule; alternatively, an average of
 from 2
 to 7 ester groups per sulfide-containing ester molecule;
 alternatively,
 an average of from 2.5 to 5 ester groups per sulfide-containing
 ester
 molecule; alternatively, an average of from 3 to 5 ester groups
 per
 sulfide-containing ester molecule; or alternatively, an average
 of from
 3 to 4 ester groups per sulfide-containing ester molecule. In yet
 other
 embodiments, the hydroxy ***thiol*** -containing ester
 comprises an
 average of about 3 ester groups per sulfide-containing ester
 molecule;
 or alternatively, an average of about 4 ester groups per
 sulfide-containing ester molecule.

DETD In some embodiments, R.sup.3 comprises at least one functional
 group.
 In one aspect, the functional group is selected from the group
 consisting of a hydroxy group, a carboxylic acid group, a
 carboxylic
 ester group, an amine group, a sulfide group, and a second
 thiol
 group. In some aspects, R.sup.3 comprises at least two functional
 groups. In some aspects, the functional groups are selected from
 the

group consisting of a hydroxy group, carboxylic acid group, a carboxylic ester group, an amine group, a sulfide group, a second ***thiol*** group, and mixtures thereof.

DETD The sulfide-containing ester compositions can also be described as a

product produced by the process comprising contacting an unsaturated ester with a ***mercaptan*** and can be further limited by the process as described herein. In other embodiments, the sulfide-containing ester composition can also be described as a product produced by a process comprising contacting an epoxidized unsaturated ester with a ***mercaptan*** and can be further limited by the process as described herein.

DETD Generally, the thioacrylate ester composition can be described as comprising thioacrylate molecules having at least one ester group in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule and at least one thioacrylate group. The ester group(s) that are in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule are hereinafter referred to as "supplementary ester group(s)." The thioacrylate ester composition described herein can be produced by contacting an acrylate composition with a ***thiol*** -containing ester composition and/or a hydroxy ***thiol*** -containing ester composition, both of which are described herein.

DETD The feedstock ***thiol*** ester compositions and/or hydroxy ***thiol*** ester compositions can comprise a mixture of molecules that have an average quantity of ester groups, ***thiol*** groups, hydroxy groups, and other groups and molar ratios described herein.

Additionally, individual ***thiol*** and hydroxy group reactivity within the ***thiol*** -containing ester compositions and/or hydroxy ***thiol*** ester compositions and statistical probability dictate

that each thioacrylate ester molecule of the thioacrylate ester composition produced may not have the same number of ester groups, thioacrylate groups, acrylate groups, and other herein disclosed quantities of functional groups, moieties, and molar ratios.

Thus, many of the properties of the thioacrylate ester molecules within the

thioacrylate ester composition are described as using an average number of the groups per thioacrylate ester molecule within the thioacrylate ester composition or as an average ratio per thioacrylate ester molecule within the thioacrylate ester composition.

DETD The thioacrylate ester can also be described as a product produced by the process that includes contacting a ***thiol*** -containing ester composition with an acrylate composition and can be further limited by the process described herein. In other embodiments, the thioacrylate ester composition can also be described as a product produced by a process that includes contacting a hydroxy ***thiol*** -containing ester composition with an acrylate composition and can be further limited by the process described herein.

DETD The present invention advantageously provides a sulfonic acid-containing ester as an embodiment of the present invention. Generally, the sulfonic acid-containing ester of the present invention includes sulfonic acid-containing ester molecules having at least one ester group and a least one sulfonic acid group. The sulfonic acid-containing ester described herein can be produced by contacting a ***thiol*** ester with an oxidizing agent as described herein. Because the feedstock for the production of the sulfonic acid-containing ester can include multiple ***thiols*** groups, ***thiol*** reactivity and statistical probability dictate that each sulfonic acid-containing ester molecule of the sulfonic acid-containing ester will not have the same number of sulfonic acid groups. Additionally, the feedstock ***thiol*** ester can also include a mixture of individual ***thiol*** ester molecules having different numbers of ***thiol*** groups and/or ester groups. Thus, many of the groups present in the sulfonic acid-containing ester are described herein as an average number of the groups per sulfonic acid-containing ester molecule or an average ratio per sulfonic acid-containing ester molecule within the sulfonic acid-containing ester.

DETD In some embodiments of the present invention, the sulfonic acid ester is substantially free of ***thiol*** groups.

DETD The sulfonic acid-containing ester can also be described as a product produced by the process comprising contacting a ***thiol***

ester

with an oxidizing agent described herein.

DETD Process for Making a ***Thiol*** Ester Composition

DETD The present invention advantageously provides processes for producing a

 thiol ester composition as embodiments of the present invention.

 As an embodiment, the present invention advantageously includes a process to produce a ***thiol*** ester composition by contacting

 hydrogen sulfide and an unsaturated ester composition containing unsaturated esters and reacting the hydrogen sulfide and unsaturated

 esters to form or produce the ***thiol*** ester composition.

As

 another embodiment of the present invention, a process to produce the

 thiol ester composition is advantageously provided. In this

 embodiment, the process includes contacting a composition comprising a

 polyol with a composition comprising a ***thiol*** containing carboxylic acid composition and reacting the polyol and

thiol
 containing carboxylic acid composition to form the ***thiol***
ester
 composition.

DETD In some embodiments of the present invention that include producing

 thiol ester compositions, the unsaturated ester composition is a

 natural source oil. In an aspect, the unsaturated ester composition is

 soybean oil or alternatively castor oil. Other suitable types of unsaturated ester compositions are described herein and can be used in

 the processes for producing the ***thiol*** ester compositions.

DETD ***Thiol*** Esters from Unsaturated Esters

DETD As an embodiment of the present invention, the ***thiol***
esters

 described herein can be produced by a process comprising contacting

 hydrogen sulfide and an unsaturated ester composition and reacting

 hydrogen sulfide and the unsaturated ester composition to form the

 thiol ester composition. In one embodiment, the unsaturated

 ester composition includes unsaturated esters having an average of at

 least 1.5 ester groups and an average of at least 1.5 carbon-carbon

 double bonds per unsaturated ester molecule. In this embodiment, the

 thiol ester composition includes ***thiol*** ester molecules

 having a molar ratio of cyclic sulfides to ***thiol*** groups of

 less than 1.5.

DETD The processes for producing the ***thiol*** ester composition can be applied to any of the unsaturated esters described herein and used to produce any of the ***thiol*** esters described herein. The process for producing the ***thiol*** ester composition can also include any additional process steps or process conditions described herein.

DETD The hydrogen sulfide to molar equivalents of unsaturated ester carbon-carbon double bonds molar ratio utilized in the process to produce the ***thiol*** ester composition can be any molar ratio that produces the desired ***thiol*** ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the equation:
$$\frac{UES\ GMW}{UES\ Mass} \times UES\ C.dbd.C$$
 In this equation, UES GMW is the average gram molecular weight of the unsaturated ester, UES Mass is the mass of the feedstock unsaturated ester, and UES C.dbd.C is the average number of double bonds per unsaturated ester molecule. In some embodiments, the ***thiol*** ester molecules have a molar ratio of the hydrogen sulfide to the unsaturated ester carbon-carbon double bonds of greater than 2. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio can be from 2 to 500; alternatively, from 5 to 200; alternatively, from 10 to 100; or alternatively, from 100 to 200.

DETD When a continuous reactor is used, a feed unsaturated ester weight hourly space velocity ranging from 0.1 to 5 can be used to produce the desired ***thiol*** ester. Alternatively, the feed unsaturated ester weight hourly space velocity ranges between 0.1 to 5; alternatively, from 0.1 to 2. Alternatively, the feed unsaturated ester weight hourly space velocity is 0.1; alternatively, the feed unsaturated ester weight hourly space velocity is 0.25; or alternatively, the feed unsaturated ester weight hourly space velocity is 2.

DETD The time required for the reaction of the unsaturated ester and hydrogen sulfide can be any time required to form the described ***thiol*** ester. Generally, the time required for the reaction of the unsaturated ester and hydrogen sulfide is at least 5 minutes.

In

some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15 minutes to 36 hours.

DETD In embodiments, the process to produce the ***thiol*** ester further comprises a step to remove excess or residual hydrogen sulfide

after reacting the hydrogen sulfide and the unsaturated ester composition. In some embodiments, the ***thiol*** ester is vacuum

stripped. In some embodiments, the ***thiol*** ester is vacuum

stripped at a temperature ranging between 25.degree. C. and 250.degree.

C.; or alternatively, between 50.degree. C. and 200.degree. C. In other

embodiments, the ***thiol*** ester is sparged with an inert gas to

remove hydrogen sulfide. In some embodiments, the ***thiol*** ester

is sparged with an inert gas at a temperature between 25.degree. C. and

250.degree. C.; or alternatively, between 50.degree. C. and 200.degree.

C. In some aspects, the inert gas is nitrogen. Generally, the stripped

or sparged ***thiol*** ester comprises less than 0.1 weight percent

hydrogen sulfide. In other embodiments, the stripped or sparged ***thiol*** ester comprises less than 0.05 weight percent

sulfur; alternatively, less than 0.025 weight percent hydrogen sulfide;

or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The reaction between the unsaturated ester and hydrogen sulfide can be

performed at any temperature capable of forming the ***thiol*** ester. In some embodiments, the unsaturated ester and hydrogen

sulfide can be reacted at a temperature greater than -20.degree. C. In other

embodiments, the unsaturated ester and hydrogen sulfide can be reacted

at a temperature greater than 0.degree. C.; alternatively, greater than

20.degree. C.; alternatively, greater than 50.degree. C.; alternatively,

greater than 80.degree. C.; or alternatively, greater than 100.degree.

C. In yet other embodiments, the unsaturated ester and hydrogen sulfide

can be reacted at a temperature from -20.degree. C. to 200.degree. C.;

alternatively, from 120.degree. C. to 240.degree. C.; alternatively,

from 170.degree. C. to 210.degree. C.; alternatively, from 185.degree.

C. to 195.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD ***Thiol*** esters having a low cyclic sulfide content can be produced using the disclosed process. In an aspect, the process for producing the ***thiol*** ester forms or produces a ***thiol*** ester having a molar ratio of cyclic sulfide to ***thiol*** groups of less than 1.5. Additional cyclic sulfide to ***thiol*** groups molar ratios are disclosed herein.

DETD In addition to lower cyclic sulfide content, ***thiol*** esters having a low carbon-carbon double bond to ***thiol*** group molar ratio can also be produced using the disclosed process. In an aspect, the process described herein produces the ***thiol*** ester having a carbon-carbon double bond to ***thiol*** group molar ratio of less than 1.5. Additional carbon-carbon double bond to ***thiol*** group molar ratios are disclosed herein.

DETD In some aspects, the process described herein produces the ***thiol*** ester molecules having an average of greater than 5 weight percent ***thiol*** sulfur. Additional ***thiol*** sulfur contents are disclosed herein. In other aspects, the process for producing a ***thiol*** ester forms a ***thiol*** ester having greater than 40 percent of the ***thiol*** ester total side chains include sulfur. Other percentages of the ***thiol*** ester total side chains that include sulfur are disclosed herein.

DETD In some embodiments, the process for producing a ***thiol*** ester composition includes contacting an unsaturated ester and hydrogen sulfide and reacting the unsaturated ester and the hydrogen sulfide to form a ***thiol*** ester. The ***thiol*** ester comprises ***thiol*** ester molecules that have a ratio of cyclic sulfide to ***thiol*** groups of less than 1.5.

DETD Tool Ester from a Polyol and a ***Thiol*** Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process to produce the ***thiol*** ester composition is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative and reacting the

polyol and ***thiol*** containing carboxylic acid and/or
thiol containing carboxylic acid derivative to produce
the
thiol ester composition. This process can be applied to
any
polyol, ***thiol*** containing carboxylic acid, or
thiol
containing carboxylic acid derivative described herein. The
process for
producing the ***thiol*** ester composition can also include
any
additional process steps or process conditions described herein.
Additionally, the process for producing the ***thiol*** ester
composition can form any ***thiol*** ester described herein.
DETD In some embodiments, the ***thiol*** ester composition
includes
thiol ester molecules that have an average of at least
1.5 ester
groups and an average of at least 1.5 ***thiol*** groups per
thiol ester molecule.
DETD The polyol used to produce the ***thiol*** ester by
contacting a
polyol and a ***thiol*** carboxylic acid and/or ***thiol***
carboxylic acid equivalent (for example a ***thiol***
carboxylic
acid methyl ester) can be any polyol or mixture of polyols that
can
produce the described ***thiol*** containing ester.
DETD In one aspect, the polyol used to produce the ***thiol***
ester can
comprise from 2 to 20 carbon atoms. In other embodiments, the
polyol
comprises from 2 to 10 carbon atoms; alternatively from 2 to 7
carbon
atoms; alternatively from 2 to 5 carbon atoms. In further
embodiments,
the polyol may be a mixture of polyols having an average of 2 to
20
carbon atoms; alternatively, an average of from 2 to 10 carbon
atoms;
alternatively, an average of 2 to 7 carbon atoms; alternatively
an
average of 2 to 5 carbon atoms.
DETD In another aspect, the polyol used to produce the ***thiol***
ester
can have any number of hydroxy groups needed to produce the
thiol ester as described herein. In some embodiments,
the polyol
has 2 hydroxy groups; alternatively 3 hydroxy groups;
alternatively, 4
hydroxy groups; alternatively, 5 hydroxy groups; or
alternatively, 6
hydroxy groups. In other embodiments, the polyol comprises at
least 2
hydroxy groups; alternatively at least 3 hydroxy groups;
alternatively,
at least 4 hydroxy groups; or alternatively, at least 5 hydroxy
groups;
at least 6 hydroxy groups. In yet other embodiments, the polyol
comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4

hydroxy groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the ***thiol*** ester is a mixture of polyols. In an embodiment, the mixture of polyols has an average of at least 1.5 hydroxy groups per polyol molecule. In other embodiments, the mixture of polyols has an average of at least 2 hydroxy groups per polyol molecule; alternatively, an average of at least 2.5 hydroxy groups per polyol molecule; alternatively, an average of at least 3.0 hydroxy groups per polyol molecule; or alternatively, an average of at least 4 hydroxy groups per polyol molecule. In yet another embodiment, the mixture of polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule; alternatively, an average of 2 to 6 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol molecule; alternatively, an average of 3 to 4 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups per polyol molecule; or alternatively, an average of 2.5 to 4.5 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the ***thiol*** ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD The ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester by contacting a polyol and a ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent can be any ***thiol*** carboxylic acid mixture comprising ***thiol*** carboxylic acids, ***thiol*** carboxylic acid equivalent or mixture comprising ***thiol*** carboxylic acid equivalents that can produce the described ***thiol*** containing ester. When talking about the characteristics ***thiol*** carboxylic acid equivalent or ***thiol*** carboxylic acid equivalents, properties such as number of carbon atoms, average number of carbon atom, molecular weight or average molecular weight, number of

thiol group, and average number of ***thiol*** groups, one will understand the these properties will apply to the portion of the ***thiol*** carboxylic acid equivalent which adds to the polyol to form the ***thiol*** ester.

DETD In an aspect, the ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester comprises from 2 to 28 carbon atoms. In an embodiment, the ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent comprises from 4 to 26 carbon atoms; alternatively, from 8 to 24 carbon atoms; alternatively, from 12 to 24 carbon atoms; or alternatively, from 14 to 20 carbon atoms. In other embodiments, a mixture comprising ***thiol*** carboxylic acid and/or mixture comprising ***thiol*** carboxylic acid equivalents has an average of 2 to 28 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 4 to 26 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 8 to 24 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 12 to 24 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; or alternatively, from 14 to 20 carbon atoms per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester has at least 1 ***thiol*** group; alternatively 2 ***thiol*** groups. In some embodiments, a mixture comprising ***thiol*** carboxylic acid and/or mixture comprising ***thiol*** carboxylic acid equivalents has an average of from 0.5 to 3 ***thiol*** groups per carboxylic acid and/or carboxylic acid equivalent; alternatively, an average of from 1 to 2 ***thiol*** groups per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent used to produce the ***thiol*** ester has a molecular weight greater than 100; alternatively greater than 180; alternatively greater than 240; or alternatively greater than 260. In other embodiments, the ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent has a molecular weight from 100 to 500; alternatively, from 120 to 420; alternatively, from 180 to 420; alternatively, from 240 to 420; a mixture or alternatively, from 260 to 360. In some embodiments, a mixture comprising ***thiol*** carboxylic acid and/or mixture

comprising ***thiol*** carboxylic acid equivalents has an average molecular weight greater than 100 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 180 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 240 per carboxylic acid and/or carboxylic acid equivalent; or alternatively greater than 260 per carboxylic acid and/or carboxylic acid equivalent.

In yet other embodiments, the mixture comprising of ***thiol*** carboxylic acid and/or mixture comprising ***thiol*** carboxylic acid equivalents has an average molecular weight from 100 to 500 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 120 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 180 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 240 to 420 per carboxylic acid and/or carboxylic acid equivalent; a mixture or alternatively, from 260 to 360 per carboxylic acid and/or carboxylic acid equivalent.

DET D In some aspects, the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative occurs in the presence of a solvent. In other aspects the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative occurs in the substantial absence of a solvent. In aspects wherein the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative occurs in the presence of a solvent, the solvent is selected from the group consisting of an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof.

Generally, the solvent, regardless of its chemical class, can include from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes the ether, the ether is diethyl

ether,
dipropyl ether, tetrahydrofuran, and any mixture thereof.

DETD When a solvent is used for the reaction between the polyol and the
the
thiol containing carboxylic acid and/or ***thiol***
containing carboxylic acid derivative, the quantity of solvent
can be
any amount that facilitates the reaction. In some embodiments,
the mass
of the solvent is less than 30 times the mass of the
thiol
containing carboxylic acid and/or ***thiol*** containing
carboxylic
acid derivative. In other embodiments, the mass of the solvent is
less
than 20 times the mass of the unsaturated ester oil;
alternatively, less
than 15 times the mass of the ***thiol*** containing
carboxylic acid
and/or ***thiol*** containing carboxylic acid derivative;
alternatively, less than 10 times the mass of the ***thiol***
containing carboxylic acid and/or ***thiol*** containing
carboxylic
acid derivative; or alternatively, less than 5 times the mass of
the
thiol containing carboxylic acid and/or ***thiol***
containing carboxylic acid derivative. In other embodiments, the
mass of
the solvent is from 2 times to 20 times the mass of the
thiol
containing carboxylic acid and/or ***thiol*** containing
carboxylic
acid derivative; alternatively, from 3 times to 15 times the mass
of the
thiol containing carboxylic acid and/or ***thiol***
containing carboxylic acid derivative; or alternatively, from 5
times to
10 times the mass of the ***thiol*** containing carboxylic
acid
and/or ***thiol*** containing carboxylic acid derivative.

DETD The equivalent of ***thiol*** containing carboxylic acid
and/or
thiol containing carboxylic acid derivative carboxylic
acid
groups to equivalents of polyol hydroxy groups molar ratio
(hereinafter
"carboxylic acid group to polyol hydroxy group molar ratio")
utilized in
the process to produce the ***thiol*** ester composition can
be any
carboxylic acid group to polyol hydroxy group molar ratio that
produces
the desired ***thiol*** ester composition. In some
embodiments, the
carboxylic acid group to polyol hydroxy group molar ratio is
greater
than 0.4. In other embodiments, the carboxylic acid group to
polyol
hydroxy group molar ratio is greater than 0.6; alternatively,
greater

than 0.8; alternatively, greater than 1; or alternatively, greater than 1.1. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio can range from 0.4 to 1.3; alternatively, from 0.6 to 1.2, or alternatively, from 0.8 to 1.1.

DETD In some aspects, the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative is catalyzed. In some embodiments, the catalyst is a mineral acid, such as sulfuric or phosphoric acid. In other embodiments, the catalyst is an organic acid. In embodiments, for example, the organic acid is methane sulfonic acid or toluene sulfonic acid.

Other suitable types of catalyst will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction of the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can occur in a batch reactor or a continuous reactor, as described herein. The reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be performed at any temperature capable of forming the ***thiol*** ester. In some embodiments, the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be reacted at a temperature greater than 20.degree. C. In other embodiments, the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be reacted at a temperature greater than 50.degree. C.; alternatively, greater than 75.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be reacted at a temperature from 20.degree. C. to 250.degree. C.; alternatively, from 50.degree. C. to 200.degree. C.; alternatively, from 75.degree. C. to 175.degree. C.; or alternatively, from 100.degree. C. to 150.degree. C.

DETD The time required for the reaction of the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can be

acid derivative can be any time required to form the described
thiol ester oil. Generally, the reaction time of the
polyol and
the ***thiol*** containing carboxylic acid and/or
thiol
containing carboxylic acid derivative is at least 5 minutes. In
some
embodiments, the reaction time is at least 30 minutes;
alternatively, at
least 1 hour; or alternatively, at least 2 hours. In yet other
embodiments, the reaction time ranges from 5 minutes to 72 hours;
alternatively, from 30 minutes to 48 hours; alternatively, from 1
hour
minutes to 36 hours; or alternatively, from 2 hours and 24 hours.
DETD When a continuous reactor is used, a feed polyol weight
unsaturated
ester weight hourly space velocity ranging from 0.1 to 5 can be
used to
produce the desired ***thiol*** ester. Alternatively, the
feed
polyol weight hourly space velocity ranges between 0.1 to 5;
alternatively, from 0.1 to 2. Alternatively, the feed polyol
ester
weight hourly space velocity is 0.1; alternatively, the feed
polyol
weight hourly space velocity is 0.25; or alternatively, the feed
polyol
weight hourly space velocity is 2.
DETD The reaction between the polyol and the ***thiol***
containing
carboxylic acid and/or ***thiol*** containing carboxylic acid
derivative can be performed at any reaction pressure that
maintains the
polyol and the ***thiol*** containing carboxylic acid and/or
thiol containing carboxylic acid derivative in a liquid
state.
In some embodiments, the reaction between the polyol and the
thiol containing carboxylic acid and/or ***thiol***
containing carboxylic acid derivative is performed at a pressure
ranging
from 0 psia to 2000 psia. In other embodiments, the reaction
pressure
ranges from 0 psia to 1000 psia; alternatively, from 0 psia and
500
psia; or alternatively, 0 psia to 300 psia.
DETD In some embodiments, the process to produce the ***thiol***
ester
by reacting a polyol and the ***thiol*** containing
carboxylic acid
and/or ***thiol*** containing carboxylic acid derivative can
further
include a step to remove excess or residual polyol, ***thiol***
containing carboxylic acid, and/or ***thiol*** containing
carboxylic
acid derivative once the polyol has reacted with the
thiol
containing carboxylic acid or ***thiol*** containing
carboxylic acid
derivative. In some embodiments, the ***thiol*** ester is
vacuum

stripped. In some embodiments, the ***thiol*** ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the ***thiol*** ester is sparged with an inert gas to remove excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative. In some embodiments, the ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged ***thiol*** ester comprises less than 5 excess polyol, ***thiol*** containing carboxylic acid, or ***thiol*** containing carboxylic acid derivative. In other embodiments, the stripped or sparged ***thiol*** ester comprises less than 2 weight percent excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative; alternatively, less than 1 weight percent excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative; or alternatively, less than 0.5 weight percent excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative.

DETD Process for Making Hydroxy ***Thiol*** Ester Composition

DETD The present invention advantageously provides processes for producing a hydroxy ***thiol*** ester as embodiments of the present invention.

As an embodiment, the present invention includes a process to produce the hydroxy ***thiol*** ester. The process comprises the steps of contacting hydrogen sulfide and an epoxidized unsaturated ester composition and reacting the hydrogen sulfide and the epoxidized unsaturated ester to form the hydroxy ***thiol*** ester. As another embodiment of the present invention, another process to produce the hydroxy ***thiol*** ester is provided. In this embodiment, the process comprises the steps of contacting a composition comprising a polyol with a composition comprising an hydroxy ***thiol*** containing carboxylic acid or an hydroxy ***thiol*** containing carboxylic acid derivative and reacting the polyol and the hydroxy ***thiol*** containing carboxylic acid or the hydroxy

thiol
containing carboxylic acid derivative to form the hydroxy
thiol
ester.

DETD Hydroxy ***Thiol*** Ester from Hydrogen Sulfide and an
Epoxidized
Unsaturated Ester Composition

DETD As an embodiment of the present invention, the hydroxy
thiol
ester composition is produced by a process comprising the steps
of
contacting hydrogen sulfide and an epoxidized unsaturated ester
composition and reacting the hydrogen sulfide and the epoxidized
unsaturated ester to produce the hydroxy ***thiol*** ester
composition.

DETD In some embodiments, the epoxidized unsaturated ester
composition
includes epoxidized unsaturated esters that have an average of at
least
1 ester groups and an average of at least 1 ***epoxide***
groups per
epoxidized unsaturated ester molecule.

DETD The process for producing or preparing the hydroxy ***thiol***
ester composition can be applied to any of the epoxidized
unsaturated
esters described herein and used to produce any hydroxy
thiol
ester described herein. The process for producing the hydroxy
thiol ester can also include any additional process
steps or
process conditions as described herein. Additionally, the process
for
producing the hydroxy ***thiol*** ester can form any hydroxy
thiol ester described herein.

DETD In some aspects, the hydroxy ***thiol*** ester is produced
by
contacting hydrogen sulfide with the epoxidized natural source
oil under
the reaction conditions to form the hydroxy ***thiol*** ester
in the
presence of an optional catalyst. In some embodiments, the
catalyst can
be a heterogeneous catalyst or a homogeneous catalyst. Examples
of
suitable catalysts are described herein. Additional types of
suitable
catalysts will be apparent to those of skill in the art and are
to be
considered within the scope of the present invention.

DETD The hydrogen sulfide to molar equivalents of ***epoxide***
groups
in the epoxidized unsaturated ester (hereinafter "hydrogen
sulfide to
epoxide group molar ratio") utilized in the process to
produce
the hydroxy ***thiol*** ester can be any hydrogen sulfide to
epoxide group molar ratio that produces the desired
hydroxy
thiol ester. The molar equivalents of epoxidized
unsaturated

ester epoxidized groups can be calculated by the equation:
 ##EQU2##
 In this equation, EUES GMW is the average gram molecular weight of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES *****Epoxide***** is the average number of *****epoxide***** groups per epoxidized unsaturated ester molecule. In some embodiments, the hydrogen sulfide to *****epoxide***** group molar ratio is greater than 0.2. In other embodiments, the hydrogen sulfide to *****epoxide***** group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to *****epoxide***** group molar ratio ranges from 0.2 to 5; alternatively, from 0.5 to 4; or alternatively, from 0.75 to 3. In some embodiments, the hydrogen sulfide to *****epoxide***** group molar ratio is greater than 2. In other embodiments, the hydrogen sulfide to *****epoxide***** group molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to *****epoxide***** group molar ratio can be from 0.2 to 500; alternatively, from 0.5 to 400; alternatively, from 1 to 300; alternatively, from 2 to 250; alternatively, 5 to 200; or alternatively, from 10 to 100.

DETD The time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide can be any time required to form the described hydroxy *****thiol***** ester. Generally, the time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide is at least 15 minutes. In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the hydroxy *****thiol***** ester composition includes hydroxy *****thiol***** ester molecules that have an average of greater than 2.5 weight percent *****thiol***** sulfur. In some embodiments, the hydroxy *****thiol***** ester composition includes hydroxy *****thiol***** ester molecules that have an average of greater than 5 weight percent *****thiol***** sulfur. Alternatively, in some

embodiments, the hydroxy ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur.

DETD In other aspects, the process producing the hydroxy ***thiol*** ester composition includes producing hydroxy ***thiol*** ester molecules having an average of greater than 40 percent of the sulfide-containing ester total side chains comprise a sulfide group.

Additional embodiments wherein the hydroxy ***thiol*** ester comprises a percentage of sulfide-containing ester total side chains are described herein.

DETD In embodiments, the process to produce the hydroxy ***thiol*** ester further comprises a step to remove residual hydrogen sulfide after reacting the hydrogen sulfide and the epoxidized unsaturated ester composition. In some embodiments, the hydroxy ***thiol*** ester is vacuum stripped. In some embodiments, the hydroxy ***thiol*** ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy ***thiol*** ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged hydroxy ***thiol*** ester comprises less than 0.05 weight percent hydrogen sulfide; alternatively, less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The reaction between the hydrogen sulfide and the epoxidized unsaturated ester can be performed at any temperature capable of forming the hydroxy ***thiol*** ester. In some embodiments, the epoxidized unsaturated ester and hydrogen sulfide can be reacted at a reaction temperature greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments,

the reaction temperature ranges from -20.degree. C. to 200.degree. C.;

alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD In another aspect, the process to produce a hydroxy ***thiol*** ester produces a hydroxy ***thiol*** ester having an ***epoxide*** group to ***thiol*** group molar ratio less than 3.3. In another aspect, the process to produce a hydroxy ***thiol*** ester produces a hydroxy ***thiol*** ester having an ***epoxide*** group to ***thiol*** group molar ratio less than 2. Other hydroxy ***thiol*** ester ***epoxide*** group to ***thiol*** group molar ratios are described herein. Alternatively, the hydroxy ***thiol*** ester ***epoxide*** group to ***thiol*** group molar ratio can be less than 1.5; alternatively, less than 1.0; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, less than 0.1.

In other embodiments, the hydroxy ***thiol*** ester can be substantially free of ***epoxide*** groups.

DETD In another aspect, the process to produce hydroxy ***thiol*** ester produces a hydroxy ***thiol*** ester wherein at least 20 percent of the side chains comprise an .alpha.-hydroxy ***thiol*** group. Other hydroxy ***thiol*** ester embodiments wherein the hydroxy ***thiol*** ester contains a percentage of side chains comprising .alpha.-hydroxy ***thiol*** groups are described herein.

DETD Hydroxy ***Thiol*** Ester from a Polyol and a Hydroxy ***Thiol*** Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process to prepare the hydroxy ***thiol*** ester is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a hydroxy ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative and reacting the polyol and hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid to form a hydroxy ***thiol*** ester composition. This process can be applied to any polyol, any hydroxy ***thiol*** containing carboxylic acid, or any ***thiol*** containing carboxylic acid derivative described herein. The process for

producing the hydroxy ***thiol*** ester composition can also include any additional process steps or process conditions described herein. Additionally, the process for producing the hydroxy ***thiol*** ester composition can form any ***thiol*** ester described herein.

DETD In some embodiments, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of at least 1 ester groups per hydroxy ***thiol*** ester molecule and an average of at least 1 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

DETD The polyol used to produce the hydroxy ***thiol*** ester by contacting a polyol and a hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent (for example a hydroxy ***thiol*** carboxylic acid methyl ester) can be any polyol or mixture of polyols that can produce the described ***thiol*** containing ester.

DETD In one aspect, the polyol used to produce the hydroxy ***thiol*** ester can comprise from 2 to 20 carbon atoms. In other embodiments, the polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7 carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments, the polyol may be a mixture of polyols having an average of 2 to 20 carbon atoms; alternatively, an average of from 2 to 10 carbon atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the hydroxy ***thiol*** ester can have any number of hydroxy groups needed to produce the hydroxy ***thiol*** ester as described herein. In some embodiments, the polyol has 2 hydroxy groups; alternatively 3 hydroxy groups; alternatively, 4 hydroxy groups; alternatively, 5 hydroxy groups; or alternatively, 6 hydroxy groups. In other embodiments, the polyol comprises at least 2 hydroxy groups; alternatively at least 3 hydroxy groups; alternatively, at least 4 hydroxy groups; or alternatively, at least 5 hydroxy groups; at least 6 hydroxy groups. In yet other embodiments, the polyol comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4 hydroxy groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the hydroxy ***thiol*** ester is a mixture of polyols. In an embodiment, the

mixture of polyols has an average of at least 1.5 hydroxy groups
 per polyol molecule. In other embodiments, the mixture of polyols has
 an average of at least 2 hydroxy groups per polyol molecule;
 alternatively, an average of at least 2.5 hydroxy groups per polyol molecule;
 alternatively, an average of at least 3.0 hydroxy groups per
 polyol molecule; or alternatively, an average of at least 4 hydroxy
 groups per polyol molecule. In yet another embodiment, the mixture of
 polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule;
 alternatively, an average of 2 to 6 hydroxy groups per polyol
 molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol
 molecule; alternatively, an average of 3 to 4 hydroxy groups per
 polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups
 per polyol molecule; or alternatively, an average of 2.5 to 4.5
 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to
 produce the hydroxy ***thiol*** ester has a molecular weight or
 average molecular weight less than 500. In other embodiments, the polyol
 or mixture of polyols have a molecular weight or average molecular
 weight less than 300; alternatively less than 200; alternatively, less
 than 150; or alternatively, less than 100.

DETD The hydroxy ***thiol*** carboxylic acid and/or hydroxy
 thiol carboxylic acid equivalent used to produce the
 hydroxy ***thiol*** ester by contacting a polyol and a hydroxy
 thiol carboxylic acid and/or hydroxy ***thiol*** carboxylic acid
 equivalent can be any hydroxy ***thiol*** carboxylic acid
 mixture comprising hydroxy ***thiol*** carboxylic acids, hydroxy
 thiol carboxylic acid equivalent or mixture comprising
 hydroxy ***thiol*** carboxylic acid equivalents that can produce the
 described hydroxy ***thiol*** containing ester. When talking about the
 characteristics hydroxy ***thiol*** carboxylic acid
 equivalent or hydroxy ***thiol*** carboxylic acid equivalents, properties
 such as number of carbon atoms, average number of carbon atom, molecular
 weight or average molecular weight, number of ***thiol*** group, and
 average number of ***thiol*** groups, one will understand the
 these properties will apply to the portion of the ***thiol***
 carboxylic

acid equivalent which adds to the polyol to form the
 thiol
 ester.

DETD In an aspect, the hydroxy ***thiol*** carboxylic acid and/or
 hydroxy ***thiol*** carboxylic acid equivalent used to
 produce the
 thiol ester comprises from 2 to 28 carbon atoms. In an
 embodiment, the hydroxy ***thiol*** carboxylic acid and/or
 hydroxy
 thiol carboxylic acid equivalents comprises from 4 to
 26 carbon
 atoms; alternatively, from 8 to 24 carbon atoms; alternatively,
 from 12
 to 24 carbon atoms; or alternatively, from 14 to 20 carbon atoms.

In
 other embodiments, a mixture comprising hydroxy ***thiol***
 carboxylic acids and/or mixture comprising hydroxy ***thiol***
 carboxylic acid equivalents has an average of 2 to 28 carbon
 atoms per
 carboxylic acid and/or carboxylic acid equivalent; alternatively,
 from 4
 to 26 carbon per carboxylic acid and/or carboxylic acid
 equivalent;
 alternatively, from 8 to 24 carbon atoms per carboxylic acid
 and/or
 carboxylic acid equivalent; alternatively, from 12 to 24 carbon
 atoms
 per carboxylic acid and/or carboxylic acid equivalent; or
 alternatively,
 from 14 to 20 carbon atoms per carboxylic acid and/or carboxylic
 acid
 equivalent.

DETD In another aspect, the hydroxy ***thiol*** carboxylic acid
 and/or
 hydroxy ***thiol*** carboxylic acid equivalent used to
 produce the
 thiol ester has at least 1 ***thiol*** group;
 alternatively
 2 ***thiol*** groups. In some embodiments, a mixture
 comprising
 hydroxy ***thiol*** carboxylic acids and/or mixture
 comprising
 hydroxy ***thiol*** carboxylic acid equivalents has an
 average of
 from 0.5 to 3 ***thiol*** groups per carboxylic acid and/or
 carboxylic acid equivalent; alternatively, an average of from 1
 to 2
 thiol groups per carboxylic acid and/or carboxylic acid
 equivalent.

DETD In another aspect, the hydroxy ***thiol*** carboxylic acid
 and/or
 hydroxy ***thiol*** carboxylic acid equivalent used to
 produce the
 thiol ester has at least 1 hydroxy group;
 alternatively, at
 least 2 hydroxy groups. In some embodiments, a mixture comprising
 hydroxy ***thiol*** carboxylic acids and/or mixture
 comprising
 hydroxy ***thiol*** carboxylic acid equivalents has an
 average of

from 0.5 to 3 hydroxy groups per carboxylic acid and/or carboxylic acid equivalent; alternatively, an average of from 1 to 2 hydroxy groups per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent used to produce the hydroxy ***thiol*** ester has a molecular weight greater than 100; alternatively greater than 180; alternatively greater than 240; or alternatively greater than 260. In other embodiments, the hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent has a molecular weight from 100 to 500; alternatively, from 120 to 420; alternatively, from 180 to 420; alternatively, from 240 to 420; a mixture or alternatively, from 260 to 360. In some embodiments, a mixture comprising hydroxy ***thiol*** carboxylic acids and/or mixture comprising hydroxy ***thiol*** carboxylic acid equivalents has an average molecular weight greater than 100 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 180 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 240 per carboxylic acid and/or carboxylic acid equivalent; or alternatively greater than 260 per carboxylic acid and/or carboxylic acid equivalent. In yet other embodiments, the mixture comprising hydroxy ***thiol*** carboxylic acid and/or mixture comprising hydroxy ***thiol*** carboxylic acid equivalents has an average molecular weight from 100 to 500 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 120 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 180 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 240 to 420 per carboxylic acid and/or carboxylic acid equivalent; a mixture or alternatively, from 260 to 360 per carboxylic acid and/or carboxylic acid equivalent.

DETD In some aspects, the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative occurs in the presence of a solvent. In other aspects, the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative occurs in the substantial absence of a solvent. In aspects wherein the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic

acid and/or hydroxy ***thiol*** containing carboxylic acid derivative occurs in the presence of a solvent, the solvent is selected from the group consisting of an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof. Generally, the solvent, regardless of its chemical class, includes from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, and any mixture thereof.

DET D When a solvent is used for the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative. In other embodiments, the mass of the solvent is less than 20 times the mass of the hydroxy ***thiol*** ester; alternatively, less than 15 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative; alternatively, less than 10 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative; or alternatively, less than 5 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative; alternatively, from 3 times to 15 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative; or alternatively, from 5 times to 10 times the mass of the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative.

acid and/or hydroxy ***thiol*** containing carboxylic acid derivative.

DETD The equivalents of hydroxy ***thiol*** containing carboxylic acid derivative and/or hydroxy ***thiol*** containing carboxylic acid derivative carboxylic acid groups to equivalents of polyol hydroxy groups molar ratio (hereinafter referred to as "carboxylic acid group to polyol hydroxy group molar ratio") utilized in the process to produce the hydroxy ***thiol*** ester can be any carboxylic acid group to polyol hydroxy group molar ratio that produces the desired hydroxy ***thiol*** ester. In some embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.4. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.6; alternatively, greater than 0.8; alternatively, greater than 1; or alternatively, greater than 1.1.

1.1. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio ranges from 0.4 to 1.3; alternatively, from 0.6 to 1.2, or alternatively, from 0.8 to 1.1.

DETD In some aspects, the reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative is catalyzed. In some embodiments, the catalyst is a mineral acid, such as sulfuric or phosphoric acid. In other embodiments, the catalyst is an organic acid. In embodiments, for example, the organic acid is methane sulfonic acid or toluene sulfonic acid. Other suitable types of catalyst will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction of the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can occur in a batch reactor or a continuous reactor, as described herein. The reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be performed at any temperature capable of forming the hydroxy ***thiol*** ester.

In some embodiments, the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic

acid derivative can be reacted at a temperature greater than 20.degree.

C. In other embodiments, the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be reacted at a temperature greater than 50.degree. C.; alternatively, greater than 75.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be reacted at a temperature from 20.degree. C. to 250.degree. C.; alternatively, from 50.degree. C. to 200.degree. C.; alternatively, from 75.degree. C. to 175.degree. C.; or alternatively, from 100.degree. C. to 150.degree..

DETD The time required for the reaction of the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be any time required to form the described hydroxy ***thiol*** ester composition. Generally, the reaction time is at least 5 minutes. In some embodiments, the reaction time is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD The reaction between the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can be performed at any reaction pressure that maintains the polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative in a liquid state. In some embodiments, the reaction pressure ranges from 0 psia to 2000 psia. In other embodiments, the reaction pressure ranges from 0 psia to 1000 psia; alternatively, from 0 psia and 500 psia; or alternatively, from 0 psia to 300 psia.

DETD In some embodiments, the process to produce the hydroxy ***thiol*** ester composition by reacting a polyol and the hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid derivative can further include a step to remove excess

or residual polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative once the polyol has reacted with the hydroxy ***thiol*** containing carboxylic acid or hydroxy ***thiol*** containing carboxylic acid derivative. In some embodiments, the ***thiol*** ester is vacuum stripped. In some embodiments, the hydroxy ***thiol*** ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas to remove excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative. In some embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C., or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy ***thiol*** ester oil comprises less than 5 excess polyol, hydroxy ***thiol*** containing carboxylic acid, or hydroxy ***thiol*** containing carboxylic acid derivative. In other embodiments, the stripped or sparged hydroxy ***thiol*** ester oil comprises less than 2 weight percent excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative; less than 1 weight percent excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative; or alternatively, less than 0.5 weight percent excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative.

DETD A method of making a thioacrylate containing ester composition is advantageously provided as another embodiment of the present invention. The process for producing the thioacrylate containing ester comprising contacting a ***thiol*** ester with an acrylate and converting at least one ***thiol*** group to a ***thiol*** acrylate group. The

process can be applied to any of the ***thiol*** esters described herein and used to any thioacrylate ester described herein. The process for producing the thioacrylate ester can also include any additional process steps or process conditions described herein.

DETD The acrylate compound can be any acrylate compound capable of reacting with a ***thiol*** group to form the ***thiol*** acrylate group.

In some embodiments, the acrylate compound can be an acrylic halide. In other embodiments, the acrylate compound can be an acrylic acid. In yet other embodiments, the acrylate compound can be an acrylic anhydride.

DETD In some aspects, the conversion of the ***thiol*** group to a thioacrylate group occurs in the presence of a solvent. In other aspects the conversion of the ***thiol*** group to a thioacrylate group occurs in the substantial absence of a solvent. In aspects wherein the conversion of the ***thiol*** group to a thioacrylate group occurs in the presence of a solvent, the solvent may be an aliphatic hydrocarbon, an ether, and aromatic compound. Generally, the solvent, regardless of its chemical class, includes from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof.

When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the conversion of the ***thiol*** group to a thioacrylate group, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the ***thiol*** ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the ***thiol*** ester; alternatively, less than 15 times the mass of the ***thiol*** ester; alternatively, less than 10 times the mass of the ***thiol*** ester; or alternatively, less than 5 times the mass

of the ***thiol*** ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the ***thiol*** ester; alternatively, from 3 times to 15 times the mass of the ***thiol*** ester; alternatively, 4 times to 15 times the mass of the ***thiol*** ester; or alternatively, from 5 times to 10 times the mass of the ***thiol*** ester.

DETD In some aspects the conversion of the ***thiol*** group to the thioacrylate group occurs in the presence of a catalyst. In some embodiments, the catalyst is homogeneous. In some embodiments, the catalyst is an organic amine. Examples of suitable organic amines include triethylamine, tripropylamine, tributylamine, and pyridine. In other embodiments, the catalyst is heterogeneous. Examples of suitable catalysts include Amberlyst A-21 and Amberlyst A-26. Other suitable catalysts will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The conversion of the ***thiol*** group to a thioacrylate group can be performed at any conversion temperature that is capable of converting the ***thiol*** group to a thioacrylate group. In some embodiments, the conversion temperature is greater than -20.degree. C. In other embodiments, the conversion temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the conversion temperature ranges from -20.degree. C. to 250.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 50.degree. C. to 150.degree. C.

DETD The conversion time required for the conversion of the ***thiol*** group to a thioacrylate group can be any time required to form the described thioacrylate containing ester. Generally, the conversion time is at least 5 minutes. In some embodiments, the conversion time is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour. In other embodiments, the conversion time ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; or alternatively, from 45 minutes to 3 hours.

DETD The conversion of the ***thiol*** group to a thioacrylate group can be performed at any conversion pressure that maintains the ***thiol*** ester and the acrylate compound in the liquid state. In some embodiments, the conversion pressure ranges from 0 psia to 2000 psia. In other embodiments, the conversion pressure ranges from 0 psia to 1000 psia; or alternatively, from 0 psia to 500 psia.

DETD Process for Producing Cross-Linked ***Thiol*** Ester

DETD As an embodiment of the present invention, a process for producing a cross-linked ***thiol*** ester composition is advantageously provided. Minimally, in some embodiments, the process to produce the cross-linked ***thiol*** ester composition comprises contacting a ***thiol*** ester composition with an oxidizing agent and reacting the ***thiol*** ester composition and an oxidizing agent to form the ***thiol*** ester oligomer having at least two ***thiol*** monomers connected by a polysulfide linkage having the structure -S.sub.Q-, wherein Q is an integer greater than 1. The disclosed method may be applied to any ***thiol*** ester described herein to produce any cross-linked ***thiol*** ester composition as described herein. The process to produce the cross-linked ***thiol*** ester composition can also include any additional process steps or process conditions as described herein.

DETD When elemental sulfur is used as the oxidizing agent, the quantity of elemental sulfur utilized to form the cross-linked ***thiol*** ester composition is determined as a function of the ***thiol*** sulfur content of the ***thiol*** ester composition. In an aspect, the weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester composition is at least 0.5. In some embodiments, the weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester composition is at least 5; alternatively, at least 10, alternatively, at least 15, or alternatively, at least 20. In other embodiments, the weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester composition ranges from 0.5 to 32; alternatively, ranges from 1 to 24; alternatively, ranges from 2 to 16; or alternatively, ranges from 3 to 10.

DETD In an aspect, the reaction of the ***thiol*** ester and

elemental sulfur occurs in the presence of a catalyst. The catalyst can be any catalyst that catalyzes the formation of the polysulfide linkage between at least two ***thiol*** ester monomers. In some embodiments, the catalyst is an amine. In further embodiments, the catalyst is a tertiary amine.

DETD The formation of the cross-linked ***thiol*** ester can occur in a batch reactor or a continuous reactor, as described herein. The formation of the cross-linked ***thiol*** ester can occur at any temperature capable of forming the ***thiol*** ester. In some embodiments, the formation of the cross-linked ***thiol*** ester can occur at a temperature greater than 25.degree. C. In other embodiments, the formation of the cross-linked ***thiol*** ester can occur at a temperature greater than 50.degree. C.; alternatively, greater than 70.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the formation of the cross-linked ***thiol*** ester occurs at a temperature from 25.degree. C. to 150.degree. C.; alternatively, from 50.degree. C. to 150.degree. C.; alternatively, from 70.degree. C. to 120.degree. C.; or alternatively, from 80.degree. C. to 110.degree. C.

DETD The time required to form the cross-linked ***thiol*** ester can be any time required to form the desired cross-linked ***thiol*** ester. Generally, the time required to form the cross-linked ***thiol*** ester is at least 15 minutes. In some embodiments, the time required to form the cross-linked ***thiol*** ester is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the time required to form the cross-linked ***thiol*** ester ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD In embodiments, the process to produce the cross-linked ***thiol*** ester further comprises a step to remove residual hydrogen sulfide. In some embodiments the cross-linked ***thiol*** ester is vacuum stripped. In some embodiments, the cross-linked ***thiol*** ester is vacuum striped at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or

alternatively, 75 and 150.degree. C. In some embodiments, the cross-linked ***thiol*** ester oil is sparged with an inert gas to remove residual hydrogen sulfide. In other embodiments, the cross-linked ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, between 75 and 150.degree. C. In yet other embodiments, the vacuum stripping is performed while sparging the cross-linked ***thiol*** ester with an inert gas. In yet other embodiments, the vacuum stripping is performed while sparging the cross-linked ***thiol*** ester an inert gas at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, 75 and 150.degree. C. In some embodiments, the inert gas is nitrogen.

DETD Generally, the stripped or sparged cross-linked ***thiol*** ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged ***thiol*** -containing ester oil comprises less than 0.05 weight percent hydrogen sulfide; alternatively, less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The present invention advantageously provides processes for producing sulfide-containing esters as embodiments of the present invention. Generally, the sulfide-containing esters can be prepared by two processes. As an embodiment of the present invention, the first process used to produce a sulfide-containing ester comprises contacting an unsaturated ester and a ***mercaptan*** and reacting the ester and ***mercaptan*** to form a sulfide-containing ester. As another embodiment of the present invention, the second process used to produce a sulfide-containing ester comprises contacting an epoxidized unsaturated ester and a ***mercaptan*** sulfide and reacting the unsaturated ester and ***mercaptan*** to form a sulfide-containing ester. Additional aspects of the two sulfide-containing ester production processes are described below.

DETD The sulfide-containing esters and sulfide-containing ester compositions described herein can be produced by a process comprising contacting a ***mercaptan*** and an unsaturated ester and reacting the

mercaptan and the unsaturated ester to form a sulfide-containing ester. The process can be applied to any of the unsaturated esters and ***mercaptans*** described herein. The process for producing the sulfide-containing ester can also include any additional process steps or process conditions described herein. Additionally, the process for producing the sulfide-containing ester can form any sulfide-containing ester described herein.

DETD In some aspects, the reaction between the ***mercaptan*** and the unsaturated ester occurs in the presence of a solvent. In other aspects the reaction between the ***mercaptan*** and the unsaturated ester occurs in the substantial absence of a solvent. When the reaction occurs in the presence of a solvent, the solvent is selected from an aliphatic hydrocarbon, an ether, an aromatic compound, an alcohol, or any combination thereof. Generally, the solvent, regardless of its chemical class, can comprise from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms. When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes an aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes an alcohol, the alcohol is methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, or any mixture thereof. When the solvent includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the ***mercaptan*** and the unsaturated ester, the quantity of solvent can be any amount that facilitates the reaction, as understood by those of skill in the art. In some embodiments, the mass of the solvent is less than 30 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester; alternatively, less than 15 times the mass of the unsaturated ester; alternatively, less than 10 times the mass of the unsaturated ester; or alternatively, less than 5 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is from 2 times to 20

times the mass of the unsaturated ester; alternatively, from 3 times to 15 times the mass of the unsaturated ester; alternatively, from 4 times to 15 times the mass of the unsaturated ester; or alternatively, from 5 times to 10 times the mass of the unsaturated ester.

DETD The molar ratio of ***mercaptan*** to molar equivalents of unsaturated ester carbon-carbon double bonds (herein after "***mercaptan*** to carbon-carbon double bond molar ratio") utilized in the process to produce the sulfide-containing ester can be any ***mercaptan*** to carbon-carbon double bond molar ratio that produces the desired sulfide-containing ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the equation: $\frac{\text{UES GMW}}{\text{UES C.dbd.C}}$ In this equation, UES GMW is the average gram molecular weight of the unsaturated ester, UES Mass is the mass of the unsaturated ester, and UES C.dbd.C is the average number of double bonds per unsaturated ester molecule. In some embodiments, the ***mercaptan*** to carbon-carbon double bond molar ratio is greater than 0.25. In other embodiments, the ***mercaptan*** to carbon-carbon double bond molar ratio is greater than 0.5; alternatively, greater than 0.75; alternatively, greater than 1; alternatively, greater than 1.25; or alternatively, greater than 1.5. In other embodiments, the ***mercaptan*** to carbon-carbon double bond molar ratio can range from 0.25 to 2; alternatively, from 0.5 to 1.5, or alternatively, from 0.75 to 1.25.

DETD In some aspects the reaction between the ***mercaptan*** and the unsaturated ester is catalyzed. The reaction of the ***mercaptan*** and the unsaturated ester can be catalyzed by a heterogeneous catalyst or homogeneous catalyst, as described herein. In some aspects, the reaction between the ***mercaptan*** and the unsaturated ester is initiated by a free radical initiator or ultraviolet radiation, as described herein.

DETD The free radical initiator can be any free radical initiator capable of forming free radicals under thermal or light photolysis. Generally, the free radical initiator is selected from the general class of compounds having a --N.dbd.N-- group or a --O-- O-- group. Specific classes of free radical initiators include diazo compounds, dialkyl peroxides, hydroperoxides, and peroxy esters. Specific initiators include

azobenzene, 2,2'-azobis(2-methylpropionitrile,
4,4'-azobis(4-cyanovaleric acid), 1,1'-azobis(cyclohexanecarbo-
nitrile),
2,2'-azobis(2methylpropane), 2,2'-azobis(2-methylpropionamidine)
dihydro-
chloride, methylpropionitrile, azodicarboxamide, tert-butyl
hydroperoxide, di-tert-butyl peroxide, octylperbenzoate. In some
embodiments, the free radical initiated reaction of the
mercaptan and the unsaturated ester is performed at a
reaction
temperature within +50.degree. C. of the 1 hour half life of the
free
radical initiator. In other embodiments, the reaction temperature
is
within .+-.25.degree. C. of the 1 hour half life of the free
radical
initiator; alternatively, the reaction temperature is within
.+-.20.degree. C. of the 1 hour half life of the free radical
initiator;
alternatively, the reaction temperature is within .+-.15.degree.
C. of
the 1 hour half life of the free radical initiator; or
alternatively,
the reaction temperature is within .+-.10.degree. C. of the 1
hour half
life of the free radical initiator. In embodiments where the free
radical initiated reaction of the ***mercaptan*** and the
unsaturated ester is initiated by light photolysis, the light can
be any
light capable creating free radicals. In some embodiments, the
light is
UV radiation. Other sources of light capable of creating free
radicals
will be apparent to those of skill in the art and are to be
considered
within the scope of the present invention.

DETD In another aspect, the reaction of the ***mercaptan*** and
the
unsaturated ester is initiated by UV radiation. In these
embodiments,
the UV radiation may be any UV radiation capable of initiating
the
reaction of the ***mercaptan*** and the unsaturated ester. In
some
embodiments, the UV radiation is generated by a medium pressure
mercury
lamp.

DETD The reaction of the ***mercaptan*** and the unsaturated
ester can
occur in a batch reactor of a continuous reactor. Any of the
batch or
continuous reactors described herein can be used in this
reaction. Other
suitable reactors will be apparent to those of skill in the art
and are
to be considered within the scope of the present invention.

DETD The reaction time for reacting the ***mercaptan*** and the
unsaturated ester can be any time required to form the
sulfide-containing ester. Generally, the reaction time is at
least 5

minutes. In some embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15 minutes to 36 hours.

DETD In some embodiments, the process to produce the sulfide-containing ester further comprises a step to remove any residual ***mercaptan*** that remains after reacting the ***mercaptan*** and the unsaturated ester. In some embodiments, the sulfide-containing ester is vacuum stripped to remove the residual ***mercaptan***. In some embodiments, the sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the sulfide-containing ester is sparged with an inert gas to remove the residual ***mercaptan***. In some embodiments, the sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged sulfide-containing ester comprises less than 5 weight percent of the ***mercaptan***. In other embodiments, the stripped or sparged sulfide-containing ester comprises less than 2 weight percent of the ***mercaptan***; alternatively, less than 1 weight percent of the ***mercaptan***; or alternatively, less than 0.5 weight percent of the ***mercaptan***.

DETD The reaction between the ***mercaptan*** and the unsaturated ester can be performed at any temperature capable of forming the sulfide-containing ester. In some embodiments, the ***mercaptan*** and the unsaturated ester can be reacted at a reaction temperature of greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the ***mercaptan*** and the unsaturated ester can be reacted at a temperature from -20.degree. C. to 250.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 80.degree. C. to 160.degree. C.

DETD The reaction between the ***mercaptan*** and the unsaturated

ester can be performed at any pressure that maintains the
mercaptan and the unsaturated ester in a substantially liquid state. In
some embodiments, the ***mercaptan*** and the unsaturated ester
can be performed at a reaction pressure ranging from 0 psig to 2000
psig. In other embodiments, the reaction pressure ranges from 0 psig to
1000 psig; alternatively, from 0 psig to 500 psig; or alternatively,
from 0 psig to 200 psig.

DETD Using the disclosed process, sulfide-containing ester having a
low carbon-carbon double bond to sulfide group molar ratio can be
produced. In an aspect, the process for producing the sulfide-containing
ester forms a sulfide-containing ester having a carbon-carbon double
bond to ***thiol*** group molar ratio of less than 1.5. Additional
carbon-carbon double bond to sulfide group molar ratios are
disclosed herein.

DETD As another embodiment of the present invention, another process
for producing a class of sulfide-containing esters, which includes
hydroxy sulfide-containing esters, is advantageously provided. In this
embodiment, the hydroxy sulfide-containing esters and hydroxy
sulfide-containing ester compositions can be produced by a
process comprising the steps of contacting a ***mercaptan*** and an
epoxidized unsaturated ester and reacting the ***mercaptan***
and the epoxidized unsaturated ester to produce or form the hydroxy
sulfide-containing ester. The process can be applied to any
mercaptan and/or any epoxidized unsaturated esters
described herein. The process for producing the hydroxy sulfide-containing
ester can also include any additional process steps or process
conditions as described herein. Additionally, the process for producing the
hydroxy sulfide-containing ester can form any hydroxy sulfide-containing
ester as described herein.

DETD In some aspects, the reaction between the ***mercaptan***
and the unsaturated ester occurs in the presence of a solvent. In other
aspects the reaction between the ***mercaptan*** and the unsaturated
ester occurs in the substantial absence of a solvent. When the reaction
occurs in the presence of a solvent, the solvent is selected from an
aliphatic

hydrocarbon, an ether, an aromatic compound, or any combination thereof.

Generally, the solvent, regardless of its chemical class, can comprise

from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms.

When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or

any mixture thereof. When the solvent includes an aromatic compound, the

aromatic compound is benzene, toluene, xylene, ethylbenzene, or any

mixture thereof. When the solvent includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the ***mercaptan***

and the epoxidized unsaturated ester, the quantity of solvent can be any

amount that facilitates the reaction, as understood by those of skill in

the art. In some embodiments, the mass of the solvent is less than 30

times the mass of the epoxidized unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of

the epoxidized unsaturated ester; alternatively, less than 15 times the

mass of the epoxidized unsaturated ester; alternatively, less than 10

times the mass of the epoxidized unsaturated ester; or alternatively,

less than 5 times the mass of the epoxidized unsaturated ester. In other

embodiments, the mass of the solvent is from 2 times to 20 times the

mass of the epoxidized unsaturated ester; alternatively, from 3 times to

15 times the mass of the epoxidized unsaturated ester; alternatively,

from 4 times to 15 times the mass of the epoxidized unsaturated ester;

or alternatively, from 5 times to 10 times the mass of the epoxidized

unsaturated ester.

DETD The reaction of the ***mercaptan*** and the epoxidized unsaturated

ester can occur using any ***mercaptan*** to molar equivalents of

epoxide groups in the epoxidized unsaturated ester (hereinafter

referred to as " ***mercaptan*** to ***epoxide*** group molar

ratio") that is capable of producing the herein described .alpha.-hydroxy ***thiol*** esters. The molar equivalents of epoxidized unsaturated ester epoxidized groups can be calculated

by the

equation: ##EQU4##

DETD In this equation, EUES GMW is the average gram molecular weight

of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES ***Epoxide*** is the average number of ***epoxide*** groups per epoxidized unsaturated ester molecule. In some embodiments, the ***mercaptan*** to ***epoxide*** group molar ratio is greater than 0.2. In other embodiments, the ***mercaptan*** to ***epoxide*** group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio ranges from 0.2 to 10; alternatively, from 0.5 to 8; alternatively, from 0.75 to 5; or alternatively, from 1 to 3.

DETD In some aspects, the reaction of the ***mercaptan*** and the epoxidized unsaturated ester occurs in the presence of a catalyst. Generally, the catalyst is any catalyst that is capable of catalyzing the reaction of the ***mercaptan*** and the epoxidized unsaturated ester to produce the desired hydroxy ***thiol*** ester. In one aspect, the catalyst is selected from the group consisting of homogeneous and heterogeneous catalysts. In other aspects, the catalyst is selected from the group consisting of zeolites, heterogeneous catalysts, homogeneous catalysts, and mixtures thereof. In another aspect, the catalyst is an amine. In other aspects, the catalyst is selected from the group consisting of cyclic conjugated amines, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-ene, and mixtures thereof.

DETD In some aspects, the reaction of the ***mercaptan*** and the epoxidized unsaturated ester occurs in the presence of a catalyst. Generally, the catalyst is any catalyst that is capable of catalyzing the reaction of the ***mercaptan*** and the epoxidized unsaturated ester to produce the desired hydroxy ***thiol*** ester. In some embodiments the catalyst is an organic base. In some embodiments, the catalyst can be 1,8-diazabicyclo[5.4.0]undec-7-ene. (What other catalysts may be used?)

DETD The reaction of the ***mercaptan*** and the epoxidized unsaturated ester can occur in a batch reactor or a continuous reactor. Any of the batch or continuous reactors described herein can be used in this reaction. Other suitable reactors will be apparent to those of skill in the art and are to be considered within the scope of the present

invention.

DETD The time required for the reaction of the ***mercaptan*** and the epoxidized unsaturated ester can be any reaction time required to form the described hydroxy sulfide-containing ester. Generally, the reaction time is at least 15 minutes. In some embodiments, the reaction time ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; or alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the process to produce the hydroxy sulfide-containing ester further comprises a step to remove the residual ***mercaptan*** after reacting the ***mercaptan*** and the epoxidized unsaturated ester. In some embodiments the hydroxy sulfide-containing ester is vacuum stripped. In some embodiments, the hydroxy sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy sulfide-containing ester is sparged with an inert gas to remove the ***mercaptan***. In some embodiments, the hydroxy sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy sulfide-containing ester comprises less than 5 weight percent of the ***mercaptan***. In other embodiments, the stripped or sparged hydroxy sulfide-containing ester comprises less than 2 weight percent of the ***mercaptan***; alternatively, less than 1 weight percent of the ***mercaptan***; or alternatively, less than 0.5 weight percent of the ***mercaptan***.

DETD The reaction between the ***mercaptan*** and the epoxidized unsaturated ester can be performed at any reaction temperature capable of forming the hydroxy sulfide-containing ester. In some embodiments, the reaction temperature is greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the reaction temperature ranges from -20.degree. C.

to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD The reaction between the ***mercaptan*** and the epoxidized unsaturated ester can be performed at any reaction pressure that maintains the ***mercaptan*** and the epoxidized unsaturated ester in a substantially liquid state. In some embodiments, the reaction pressure ranges from 0 psig to 2000 psig. In other embodiments, the reaction pressure ranges from 0 psig to 1000 psig; alternatively, from 0 psig to 500 psig; or alternatively, from 0 psig to 200 psig.

DETD In another aspect, the process to produce a hydroxy sulfide-containing ester produces a hydroxy sulfide-containing ester having an ***epoxide*** group to sulfide group molar ratio less than 2.

Other hydroxy sulfide-containing ester ***epoxide*** group to sulfide group molar ratios are described herein. (The next passage needs to be incorporated into the hydroxy ***thiol*** ester section along with the first sentence of this paragraph.) Alternatively, the hydroxy sulfide-containing ester ***epoxide*** group to ***thiol*** group molar ratio can be less than 1.5; alternatively, less than 1.0; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, less than 0.1. In other embodiments, the hydroxy sulfide-containing ester can be substantially free of ***epoxide*** groups.

DETD As an embodiment of the present invention, processes for producing a sulfonic acid-containing ester and for producing a sulfonate-containing ester are advantageously provided. Generally, the process for producing the sulfonic acid-containing ester comprises the steps of contacting a ***thiol*** ester and an oxidizing agent and oxidizing at least one ***thiol*** group of the ***thiol*** ester to produce a sulfonic acid group. The process for producing the sulfonate-containing ester comprises the steps of contacting a sulfonic acid-containing ester with a base and forming a sulfonate-containing ester.

DETD In an embodiment, the process to prepare a sulfonic acid-containing ester comprises the steps of contacting the ***thiol*** ester and the oxidizing agent and oxidizing the ***thiol*** ester to produce the sulfonic acid-containing ester. Generally the oxidizing agent oxidizes at least one ***thiol*** group of the ***thiol***

ester to a sulfonate group. The process to produce the sulfonic acid-containing ester composition can be applied to any ***thiol*** ester described herein to prepare any sulfonic acid-containing ester described herein. In some embodiments, the ***thiol*** ester includes a hydroxy group. For example, the ***thiol*** ester can be any hydroxy ***thiol*** ester described herein. The oxidizing agent can be any oxidizing agent described herein.

DETD In some aspects, the oxidation of the ***thiol*** ester occurs in the presence of a solvent. In some aspects, the solvent is water.

DETD The oxidizing agent that is contacted with the ***thiol*** ester can be any oxidizing agent capable of oxidizing a ***thiol*** group to a sulfonic acid group. In some embodiments, the oxidizing agent is oxygen. In other embodiments, the oxidizing agent is chlorine. In other embodiments, the oxidizing agent is dimethyl sulfoxide. In yet other embodiments, the oxidizing agent is a combination of a hydrogen halide and a catalytic amount of a dialkyl sulfide, such as dimethyl sulfoxide.

Other suitable oxidizing agents will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The oxidation of the ***thiol*** ester can be performed at any temperature capable of converting the ***thiol*** ester to a sulfonic acid-containing ester. In some embodiments, the ***thiol*** ester is oxidized at a temperature greater than -20.degree. C. In other embodiments, the ***thiol*** ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively, greater than 50.degree. C.

DETD The time required for the oxidation of the ***thiol*** ester can be any time required to form the desired sulfonic acid-containing ester. Generally, the time required for the oxidation of the ***thiol*** ester is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour.

In some embodiments, the time required for the oxidation of the ***thiol*** ester ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; alternatively, from 45 minutes to 3 hours.

DETD The oxidation of the ***thiol*** ester can be performed at

any pressure that maintains the ***thiol*** ester and the oxidation agent in the proper state, which is not always a liquid state, to oxidize the ***thiol*** ester to a sulfonic acid-containing ester. For example, when the oxidation agent is chlorine, the chlorine can be in the gaseous state. In some embodiments, the oxidation of the ***thiol*** ester can be performed at a pressure ranging from 0 psig to 2000 psig. In other embodiments, the oxidation of the ***thiol*** ester can be performed at a pressure ranging from 0 to 1000 psig; or alternatively, 0 to 500 psig.

DETD The oxidation of the ***thiol*** ester can be performed in a batch reactor or a continuous reactor, as described herein. Additionally, the process to produce the sulfonic acid-containing ester can comprise additional process steps as recognized by those skilled in the art.

DETD The formation of the sulfonate-containing ester can be performed at any temperature capable of converting the sulfonic acid group of the sulfonic acid-containing ester to a sulfonate group. In some embodiments, the sulfonate-containing ester is formed at a temperature greater than -20.degree. C. In other embodiments, the ***thiol*** ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively, greater than 50.degree. C. In yet other embodiments, the ***thiol*** ester is oxidized at a temperature ranging from 0.degree. C. to 250.degree. C.; alternatively, from 0.degree. C. to 150.degree. C.; or alternatively, from 20.degree. C. to 100.degree. C.

DETD A preferred sulfur-containing vegetable oil is MVO available from Chevron Phillips Chemical Co. under the tradename Polymercaptan 358. Polymercaptan 358 is made by the free radical addition of hydrogen sulfide to the double bonds in soybean oil. Typically, Polymercaptan 358 has a ***thiol*** sulfur content of 5 to 10% and equivalent weights of 640 to 320, respectively.

DETD Another preferred sulfur-containing vegetable oil useful as part of the isocyanate-reactive component is a MHVO such as mercapto-hydroxy soybean oil. As described herein, a preferred mercapto-hydroxy soybean oil is made by the free radical addition of hydrogen sulfide to epoxidized

soybean oil. Typically, the mercapto and hydroxy functionalities are equal and the ***mercaptan*** content is about 8.3% ***thiol*** sulfur. The equivalent weight of this material is 192, which includes both mercapto and hydroxy functionalities.

DETD Yet another preferred sulfur-containing vegetable oil useful as part of the isocyanate-reactive component is a CMVO such as sulfur cross-linked mercaptanized soybean oil. Sulfur cross-linked mercaptanized soybean oil is made by the addition of elemental sulfur to mercaptanized soybean oil. In this process, a portion of the ***mercaptan*** groups are consumed as cross-linking sites for the sulfur. Typical sulfur cross-linked mercaptanized soybean oil products by Chevron Phillips Chemical Co. include Runs #22, 194, 195, 196 and 197 and have a ***thiol*** sulfur content ranging from about 8.0% to 1.4% and equivalent weights ranging from about 400 to about 2250, respectively.

DETD For epoxy polymer encapsulated CRF material made from sulfur-containing vegetable oil, it has been found that the use of a tertiary amine catalyst is highly preferred. The amount used is such to be sufficient to give the desired reaction rate for the production of the encapsulated slow release fertilizer product. A non-limiting example of a suitable amine catalyst is diazobicycloundecacene also known as 1,8-diazabicyclo[5,4,0]undec-7-ene [CAS# ***6674-22-2***] or "DBU", which is preferably used in the range of about 0.1% to 0.5% by weight of the coating. Other suitable catalyst materials will be apparent to those of ordinary skill in the art.

DETD The preferred sulfur-containing vegetable oil to be used in production of an epoxy polymer coated CRF material is MHVO such as mercapto-hydroxy soybean oil. One such material is mercapto-hydroxy soybean oil known as MHSO 566-84 produced by Chevron Phillips Chemical Co. This preferred material contains 8.33% ***thiol*** sulfur, with an equivalent weight of 384, based upon the ***mercaptan*** functionality.

DETD The unsaturated ester used as a feedstock to produce the ***thiol*** ester compositions described herein can be described using a number of different methods. One method of describing the unsaturated ester feedstock is by the number of ester groups and the number of carbon-carbon double bonds that comprise each unsaturated ester

oil

molecule. Suitable unsaturated ester used as a feedstock to produce the ***thiol*** ester compositions described herein minimally comprise at least 1 ester group and at least 1 carbon-carbon double bond. However, beyond this requirement, the number of ester groups and carbon-carbon double bonds comprising the unsaturated esters are independent elements and can be varied independently of each other. Thus, the unsaturated esters can have any combination of the number of ester groups and the number of carbon-carbon double bonds described separately herein. Suitable, unsaturated esters can also contain additional functional groups such as alcohol, aldehyde, ketone, epoxy, ether, aromatic groups, and combinations thereof. As an example, the unsaturated esters can also comprise hydroxy groups. An example of an unsaturated ester that contains hydroxy groups is castor oil. Other suitable unsaturated esters will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the unsaturated ***thiol*** ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD In some embodiments, suitable polyols include 1,2-ethanediol, 1,3-propanediol, 1,4- ***butanediol***, 1,5-pentanediol, 1,6-hexanediol, dimethylolpropane, neopentylpropane, 2-propyl-2-ethyl-1,3-propanediol, 1,2-propanediol, 1,3- ***butanediol***, diethylene glycol, triethylene glycol, polyethylene glycol, dipropylene glycol, tripropylene glycol, and polypropylene glycol; cyclohexanedimethanol, 1,3-dioxane-5,5-dimethanol; and 1,4-xylylenedimethanol and 1-phenyl-1,2-ethanediol, trimethylolpropane, trimethylolethane, trimethylolbutane, glycerol, 1,2,5-hexanetriol, pentaerythritol, ditrimethylolpropane, diglycerol, ditrimethylolethane, 1,3,5-trihydroxybenzene, 1,4-xylylenedimethanol, and 1-phenyl-1,2-ethanediol, or any combination thereof. In further embodiments, the polyol is glycerol, pentaerythritol, or mixtures thereof. In other embodiments, the polyol is glycerol, or alternatively pentaerythritol.

DETD Specific carboxylic acids used as a component of the carboxylic acid composition used to produce the unsaturated ester oil can have from 3 to 30 carbon atoms per carboxylic acid molecule. In some embodiments the carboxylic acid is linear. In some embodiments the carboxylic acid is branched. In some embodiments the carboxylic acid is a mixture of linear and branched carboxylic acids. In some embodiments the carboxylic acid can also comprise additional functional groups including alcohols, aldehydes, ketones, and ***epoxides***, among others.

DETD Minimally, the epoxidized unsaturated ester comprises at least one ***epoxide*** group. In an embodiment the epoxidized unsaturated ester comprises at least 2 ***epoxide*** groups; alternatively, at least 3 ***epoxide*** groups; or alternatively, at least 4 ***epoxide*** groups. In other embodiments, the epoxidized unsaturated ester comprises from 2 to 9 ***epoxide*** groups; alternatively, from 2 to 4 ***epoxide*** groups; alternatively, from 3 to 8 ***epoxide*** groups; or alternatively, from 4 to 8 ***epoxide*** groups.

DETD In some embodiments, the unsaturated ester comprises a mixture of epoxidized unsaturated esters. In this aspect, the number of ***epoxide*** groups in the epoxidized unsaturated ester is best described as an average number of ***epoxide*** groups per epoxidized unsaturated ester molecule. In some embodiments, the epoxidized unsaturated esters have an average of at least 1.5 ***epoxide*** groups per epoxidized unsaturated ester molecule; alternatively, an average of at least 2 ***epoxide*** groups per epoxidized unsaturated ester molecule; alternatively, an average of at least 2.5 ***epoxide*** groups per epoxidized unsaturated ester molecule; or alternatively, an average of at least 3 ***epoxide*** groups per epoxidized unsaturated ester molecule. In other embodiments, the epoxidized unsaturated esters have average of from 1.5 to 9 ***epoxide*** groups per epoxidized unsaturated ester molecule; alternatively, an average of from 3 to 8 ***epoxide*** groups per epoxidized unsaturated ester molecule; alternatively, an average of from 2 to 4 ***epoxide*** groups per epoxidized unsaturated ester molecule; or alternatively, from of 4 to 8 ***epoxide*** groups per epoxidized unsaturated ester molecule.

DETD The ***thiol*** composition can include an average of greater than 0 to about 4 ***epoxide*** groups per triglyceride. The ***thiol*** composition can also include an average of greater than 1.5 to about 9 ***epoxide*** groups per triglyceride.

DETD ***Mercaptans***

DETD Within some embodiments, an unsaturated ester or an epoxidized unsaturated ester is contacted with ***mercaptan***. Within these embodiments, the ***mercaptan*** can be any ***mercaptan*** comprising from 1 to 20 carbon atoms. Generally, the ***mercaptan*** can have the following structure: $HS-R^{sup.3}$ wherein R³ is a C1 to C20 organyl groups or a C1 to C20 hydrocarbyl groups. In further embodiments the R³ can be a C2 to C10 organyl group or a C2 to C10 hydrocarbyl group. In some embodiments, the ***mercaptan*** composition comprises a solvent. In one aspect, the ***mercaptan*** composition comprises at least one other functional group.

DETD The at least one other functional group can be selected from several different groups. For example, the at least one other functional group is an alcohol group, a carboxylic alcohol group, a carboxylic ester group, an amine group, a sulfide group, a ***thiol*** group, a methyl or ethyl ester of a carboxylic acid group, or combinations thereof. Other types of functional groups will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In some embodiments, the ***mercaptan*** is selected from the group consisting of 3-mercaptopropyl-trimethoxysilane, 2-mercaptopyridine, 4-mercaptopyridine, 2-mercaptopyrimidine, mercaptopyruvic acid, mercaptosuccinic acid, 2-mercaptonicotinic acid, 6-mercaptonicotinic acid, 2-mercaptophenol, 4-mercaptophenol, 3-mercapto-1,2-propanediol, 3-mercapto-1,2-propanediol, 3-mercapto-1-propanesulfonic acid, 1-mercapto-2-propanol, 3-mercapto-1-propanol, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzyl alcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 2-mercaptoethanesulfonic acid, 2-mercaptoethanol, 2-mercaptoethyl ether, 2-mercaptoethyl sulfide, 16-mercaptohexadecanoic acid, 6-mercapto-1-hexanol, 4'-mercaptoacetanilide, mercaptoacetic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, 2-mercaptothiazoline, 3-mercapto-1H-1,2,4-triazole, 11-mercaptoundecanoic acid, 11-mercapto-1-undecanol, or combinations thereof.

DETD In some embodiments, the ***mercaptan*** is selected from

the group

consisting of beta-mercaptoethanol, 2-mercaptophenol, 3-mercaptophenol, 4-mercaptophenol, 1-mercapto-2-propanol, 1-mercapto-3-propanol, mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, 2-mercaptobenzylalcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 2-mercaptoethyl ether, 2-mercaptoethyl sulfide, 6-mercapto-hexanol, 3-mercapto-1,2-propanediol, mercaptosuccinic acid, and mixtures thereof.

In further embodiments, the ***mercaptan*** is selected from the

group consisting of beta-mercaptoethanol, 1-mercapto-2-propanol, 1-mercapto-3-propanol, 2-mercaptobenzylalcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 6-mercapto-hexanol, 3-mercapto-1,2-propanediol,

and mixtures thereof. In further embodiments, the ***mercaptan*** is

selected from the group consisting 2-mercaptophenol, 3-mercaptophenol, 4-mercaptophenol, and mixtures thereof. In yet further embodiments, the

mercaptan is selected from the group consisting mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, mercaptosuccinic acid, and mixtures thereof.

DETD Within some embodiments, the inventive compositions described herein

are reacted with an isocyanate compound to produce a polythiourethane

composition. The isocyanate may be any isocyanates capable of reacting

with the ***thiol*** esters, hydroxy ***thiol*** esters, and a

cross-linked ***thiol*** esters described herein to form a polyurethane composition. Generally, the isocyanate compound has

at least two isocyanate groups.

DETD In order to quantitatively measure the ***thiol*** sulfur, the

thiol sulfur analyses were conducted using silver nitrate

titration in accordance with ASTM D3227, with the following modifications designed to minimize probe fouling by silver salts:

the samples were diluted in a known mass of tetrahydrofuran. The

silver nitrate concentration was 0.01 N standardized against potassium iodide.

DETD ***Thiol*** sulfur was analyzed by three different tests.

The first

test used was the modified ASTM D3227, which resulted in a ***thiol***

sulfur measurement of 4.64%. The second test used to measure the
 thiol sulfur was SLP-1204, which is a test developed by
 Chevron
 Phillips Chemical Company LLP. By using the SLP-1204 test, the
 resulting
 thiol sulfur measurement was 4.28%. Lastly, the total
 sulfur was
 measured by combustion analysis, which resulted in a total sulfur
 measurement of 4.27%.
 DETD Vegetable oil (42 kg) was charged to a 100-gallon holding
 vessel. The
 vessel was purged with nitrogen and returned to atmospheric
 pressure.
 Hydrogen sulfide (174 kg) was charged to the holding vessel. The
 vessel
 temperature was controlled from 25-30.degree. C. while the
 pressure was
 typically maintained between 380-400 psig. The reactants were
 continuously rolled from the holding tank through a stainless
 steel
 tubular photochemical reactor containing a 7.5 KW Hanovia medium
 pressure mercury lamp contained within a quartz tube. Reactor
 temperature, pressure, and composition were monitored over the
 course of
 the reaction. The reaction time was dependent upon reaching a
 desired
 composition of ***thiol*** sulfur. Upon completion, the
 unreacted
 hydrogen sulfide was slowly vented from the system. Residual
 H.sub.2S
 was removed at 100.degree. C. and reduced pressure while passing
 nitrogen through a nitrogen sparge tube. The product was drained
 from
 the bottom of the reactor into a clean drum. The ***thiol***
 sulfur
 measurements were 11.0% when using the modified ASTM D3227, 8.74%
 when
 using SLP-1204, and the total sulfur was 11.21% when using
 combustion
 analysis (total sulfur).
 DETD The resulting mercaptanized soybean oil was subjected to
 nitrogen
 sparging under reduced pressure at 100.degree. C. for a period of
 4
 hours to remove any residual hydrogen sulfide. The ***thiol***
 sulfur measurements were 13.0% when using the modified ASTM
 D3227, 9.82%
 when using SLP-1204, and 11.69% when using combustion analysis.
 DETD Table 1 provides the properties of the mercaptanized soybean oil
 produced in examples 1-3.
 TABLE 1

Mercaptanized Soybean Oil Product Properties

	Cyclic Sulfide to ***Thiol*** Sulfur.sup..dagger. Group	***Thiol*** to groups	Molar Ratio	Molar Ratio
C.dbd.C				
Example	(wt %)			

1	4.28	0.02	2.79
2	11.0	0.03	0.26
3	13.0	0.03	0.51

.sup..dagger. ***Thiol*** sulfur content determined by the modified ASTM

D3227

DETD Soybean oil was charged to a 1000 gallon stirred reactor.

Hydrogen

sulfide was then charged to the reactor. After the hydrogen sulfide was

charged to the reactor, the stirrers and the UV lamps were turned on and

the reaction allowed to build temperature and pressure as the reaction

proceed. The reaction was continued until a minimum ***thiol*** sulfur content of 8 weight percent was achieved. After reaction was

completion, the excess hydrogen sulfide was flashed from the reactor.

For runs 2-5, the mercaptanized soybean oil product underwent an additional hydrogen sulfide stripping step comprising stripping hydrogen

sulfide from the product under vacuum, 50 mm Hg, at 250.degree.

F. (only

true for runs 2-5).

DETD Table 3 provides the details of the analysis of the mercaptanized

soybean oil producing in the five 1000 gallon reactor runs.

TABLE 3

1000 gallon reactor Mercaptanized Soybean Oil Product Properties

	Thiol	Cyclic Sulfide to	***Thiol***	Side Chain C.dbd.C
to				

Run	***Thiol*** Sulfur.sup..dagger. ***Thiol*** (wt %)	Containing Group Groups Molar Ratio	groups Molar Ratio	(%)
1	9.3	--	--	71.6
2	9.6	0.04	0.48	72.3
3	9.2	0.03	0.59	69.1
4	9.3	0.03	0.62	71.6
5	10.1	0.03	0.54	72.3

.sup..dagger. ***Thiol*** sulfur content determined by Raman

spectroscopy

Mercaptanized Castor Bean Oil

DETD The analytical properties of the two mercaptanized castor oil products

are provide in Table 4.

TABLE 4

Mercaptanized Castor Oil Product Properties

Containing	***Thiol*** Sulfur.sup..dagger.	C.dbd.C to	Side Chain groups

Thiol

Groups

Example	(wt %)	Molar Ratio	(%)
1	6.4	0.52	64.1
2	7.4	0.26	77.7

.sup..dagger. ***Thiol*** sulfur content determined by Raman spectroscopy

Mercaptohydroxy Soybean Oil Synthetic Procedure

DETD Epoxidized Soybean Oil (700 g, .about.0.7 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 4.7 g, 30.5 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 132.0 g, 3.87 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 8 hrs, during which time the reactor pressure decreased from a maximum of 351 psig to 219 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 7.53

wt. %, 2.5 SH/molecule, or 2.35 meq SH/g. Combustion analysis indicated C, 64.37%; H, 10.20%; N, <0.15%; and S, 9.51%.

DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 97.degree. C. with stirring for 14 hrs, during which time the reactor pressure decreased from a maximum of 509 psig to 229 psig. The stirrer was stopped and while still warm (90-95.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under

vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content of 4.14 wt. %, 1.4 SH/molecule, or 1.29 meq SH/g. Combustion analysis indicated C, 65.18%; H, 10.17%; N, <0.15%; and S, 7.80%.

DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 10 hrs, during which time the reactor pressure decreased from a maximum of 578 psig to 489 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration with modified ASTM D3227) content of 8.28 wt. %, 2.8 SH/molecule, or 2.58 meq SH/g. Combustion analysis indicated C, 65.24%; H, 9.52%; N, 0.18%; and S, 9.53%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 12 hrs, during which time the reactor pressure decreased from a maximum of 587 psig to 498 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a
thiol sulfur (titration by modified ASTM D3227) content
of 8.24

wt. %, 2.8 SH/molecule, or 2.57 meq SH/g. Combustion analysis
indicated

C, 63.39%; H, 10.01%; N, <0.15%; and S, 8.76%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were
charged

to a 1-L Hastelloy C autoclave reactor, and the vessel was
pressure

tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99
mol) was

then pressured into the stirred reactor contents through a dip
tube in

the liquid space. The reaction mixture was heated and maintained
at

85.degree. C. with stirring for 8 hrs, during which time the
reactor

pressure decreased from a maximum of 606 psig to 537 psig. The
stirrer

was stopped and while still warm (80-85.degree. C.), excess
H.sub.2S was

slowly vented to a low-pressure flare. The reactor vapor space
was then

swept with N.sub.2 for 1 hr and the reactor contents drained warm
(80-85.degree. C.). The reaction product was N.sub.2 sparged

under
vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove
residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a
thiol sulfur (titration by modified ASTM D3227) content
of 7.34

wt. %, 2.5 SH/molecule, or 2.29 meq SH/g. Combustion analysis
indicated

C, 64.47%; H, 10.18%; N, <0.15%; and S, 8.40%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were
charged

to a 1-L Hastelloy C autoclave reactor that was pressure tested
to 630

psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then
pressured

into the stirred reactor contents through a dip tube in the
liquid

space. The reaction mixture was heated and maintained at
85.degree. C.

with stirring for 6 hrs, during which time the reactor pressure
decreased from a maximum of 586 psig to 556 psig. The stirrer was
stopped and while still warm (80-85.degree. C.), excess H.sub.2S

was
slowly vented to a low-pressure flare. The reactor vapor space
was then

swept with N.sub.2 for 1 hr and the reactor contents drained warm
(80-85.degree. C.). The reaction product was N.sub.2 sparged

under
vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove
residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a
thiol sulfur (titration by modified ASTM D3227) content

of 5.93

wt. %, 2.0 SH/molecule, or 1.85 meq SH/g. Combustion analysis indicated

C, 65.26%; H, 10.19%; N, <0.15%; and S, 8.43%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure

tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was

then pressured into the stirred reactor contents through a dip tube in

the liquid space. The reaction mixture was heated and maintained at

85.degree. C. with stirring for 4 hrs, during which time the reactor

pressure decreased from a maximum of 595 psig to 554 psig. The stirrer

was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was

slowly vented to a low-pressure flare. The reactor vapor space was then

swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged

under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a

thiol sulfur (titration by modified ASTM D3227) content

of 5.36

wt. %, 1.8 SH/molecule, or 1.67 meq SH/g. Combustion analysis indicated

C, 65.67%; H, 10.17%; N, 0.34%; and S, 9.84%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630

psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured

into the stirred reactor contents through a dip tube in the liquid

space. The reaction mixture was heated and maintained at 85.degree. C.

with stirring for 4 hrs, during which time the reactor pressure decreased from a maximum of 577 psig to 519 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S

was slowly vented to a low-pressure flare. The reactor vapor space was then

swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged

under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a

thiol sulfur (titration with AgNO.sub.3) content of

5.85 wt. %,

2.0 SH/molecule, or 1.82 meq SH/g. Combustion analysis indicated

C, 65.09%; H, 10.15%; N, 0.35%; and S, 10.63%.
 DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and
 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were
 charged to a 1-L Hastelloy C autoclave reactor, and the vessel was
 pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99
 mol) was then pressured into the stirred reactor contents through a dip
 tube in the liquid space. The reaction mixture was heated and maintained
 at 85.degree. C. with stirring for 2 hrs, during which time the
 reactor pressure decreased from a maximum of 577 psig to 508 psig. The
 stirrer was stopped and while still warm (80-85.degree. C.), excess
 H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space
 was then swept with N.sub.2 for 1 hr and the reactor contents drained warm
 (80-85.degree. C.). The reaction product was N.sub.2 sparged
 under vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove
 residual H.sub.2S. The resulting light yellow, viscous sticky oil had a
 thiol sulfur (titration by modified ASTM D3227) content
 of 5.07 wt. %, 1.7 SH/molecule, or 1.58 meq SH/g. Combustion analysis
 indicated C, 63.96%; H, 10.01%; N, 0.35%; and S, 11.22%.
 DETD Table 5 provides the properties of the mercaptohydroxy soybean
 oil samples produced in Examples 1-10.

TABLE 5

Mercaptan					
Epoxides					
per	Reaction	Reaction	Sulfur	SH per	groups left
Epoxide :SH					
Example	Time (hrs)	Temp (.degree. C.)	(wt. %).1	molecule.2	
	molecule.3	Molar Ratio			
1	0	N/A	N/A	0	4.3
--					
2	8	85	7.53	2.5	1.8
	0.72				
3	14	97	4.14	1.4	2.9
	2.07				
4	10	85	8.28	2.8	1.5
	0.54				
5	12	85	8.24	2.8	1.5
	0.54				
6	8	85	7.34	2.5	1.8
	0.72				
7	6	85	5.93	2.0	2.3

8	1.15 4	85	5.36	1.8	2.5
9	1.40 4	85	5.85	2.0	2.3
10	1.15 2	85	5.07	1.7	2.6
	1.529				

.sup.1Thiol sulfur was determined by silver nitrate oxidation using ASTM D 3227

.sup.2Determined by Wt. % ***thiol*** sulfur

.sup.3Determined by subtracting the SH/molecule from the starting material

epoxide content

DETD Epoxidized soybean oil and the catalyst were charged to a 1-L Hastelloy

C autoclave reactor, and the vessel was pressure tested to 1000 psig.

Hydrogen sulfide was then pressured into the stirred reactor contents

through a dip tube in the liquid space. The reaction mixture was heated

and maintained at temperature a set period of time with stirring for 12

hrs. During the reaction time the reactor pressure usually decreased. At

the end of the reaction time, the stirrer was stopped and excess H.sub.2S was slowly vented while the reaction mixture was warm to a

low-pressure flare. The reactor vapor space was then swept with N.sub.2

for 1 hr and the reactor contents drained. The reaction product was

N.sub.2 sparged under vacuum (<50 mmHg) at 100.degree. C. for 16 hrs to

remove residual H.sub.2S. Table 6 provides the reaction conditions used

to produce the mercaptohydroxy soybean oils for several runs and the

thiol sulfur content of the mercaptohydroxy soybean oils

produced.

TABLE 6

Mecaptohydroxy Soybean Oil Production Runs

Run (minutes)	Epoxidized Soybean Oil		Catalyst (g)	H.sub.2S (g)	H.sub.2S: Molar Ratio	***Epoxide*** Sulfur.sup.a (.degree. C.)
	Temperature (g)	Time (wt. %)				
556-41.sup.. 728	dagger. 249.6 5.69		1.950	214.0	5.86	64
556-53.sup.. 370	dagger. 250.0 9.04		2.000	213.0	5.81	100
556-47.sup.. 720	dagger. 250.5 10.47		1.050	213.0	5.81	101
407-81D.sup.. 	dagger. 500.0		4.200	255.0	3.49	85

480	7.53				
407-86.sup..dagger.	600.0	5.000	204.0	2.07	85
600	8.28				
556-79.sup..dagger-dbl.	250.0	2.600	214.0	5.83	100
720	6.68				
556-80.sup..dagger-dbl.	251.0	5.000	214.0	5.81	100
720	9.51				

.sup..dagger.Catalyst was DBU
 .sup..dagger-dbl.catalyst was triethylamine (TEA)
 .sup.aThiol sulfur measured by silver nitrate titration using modified ASTM D

3227

DETD Run number 407-86 was subjected to the sodium methoxide methanolysis procedure and subsequently analyzed by GC/MS. The GC/MS analysis indicated that the product had ***epoxide*** group to ***thiol*** group molar ratio of approximately 0.14. The methanolysis data also indicated that an average of 80.4 percent of the product mercaptohydroxy soybean oil contained sulfur.

DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur pellets (9.6 g). The reaction mixture was heated to 120.degree. C. until sulfur dissolved and then cooled to 99.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs.

H.sub.2S evolution was observed. The reaction product (904.8 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a ***thiol*** sulfur of 6.33 wt. % (by modified ASTM D3227). The elemental combustion analysis was 70.19%; C, 10.37%; H, and 11.21%; S.

DETD Mercaptanized soybean oil (900.0 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur pellets (36.0 g). The reaction mixture was heated to 120.degree. C. until sulfur dissolved and then cooled to 100.degree. C.

Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 36 hrs. H.sub.2S evolution was observed. The reaction product (825.6 g) was sparged with N.sub.2 under vacuum at 90.degree. C. for 36 hrs to remove residual H.sub.2S. The reaction product was then sparged with N.sub.2 under vacuum at 110.degree. C. for 3 hrs to remove residual

H.sub.2S.

The final product was a light yellow oil with a ***thiol*** sulfur of 2.36 wt. % (by modified ASTM D3227). The elemental combustion analysis was 68.90%; C, 11.07%; H, and 12.25%; S. DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur pellets (18.0 g). The reaction mixture was heated to 125.degree. C.

until sulfur dissolved and then cooled to 101.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H.sub.2S evolution was observed. The reaction product (901.5 g)

was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a

thiol sulfur of 4.9 wt. % (by modified ASTM D3227). The elemental combustion analysis was 69.58%; C, 11.25%; H, and 11.31%; S.

DETD Mercaptanized soybean oil (900.2 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur pellets (45.0 g). The reaction mixture was heated to 125.degree. C.

until sulfur dissolved and then cooled to 100.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H.sub.2S evolution was observed. The reaction product (915.0 g)

was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a

thiol sulfur of 1.41 wt. % (by modified ASTM D3227).

The elemental combustion analysis was 68.35%; C, 10.98%; H, and 13.28%; S.

DETD Numerous polythiourethane compositions were prepared by reacting a

thiol ester composition with a diisocyanate in the presence of a catalyst by using the processes described herein for preparing such

polythiourethane compositions. The compositions were produced using the different variables of feedstocks, diisocyanates, stoichiometry, and

catalysts shown in Table 8. Once every combination of variable was used, over 1200 compositions were produced. Each of the feedstocks were reacted with each of the diisocyanates at each of the stoichiometries

with each of the catalysts listed to produce the 1200+

compositions. The stoichiometry was based upon a ***thiol*** ester composition (MSO, MHSO, CMSO, MCO) active hydrogen (***thiol*** and hydroxyl group) to diisocyanate equivalent ratio. For example, castor oil was reacted with toluene diisocyanate at a stoichiometric value of 1.25 while using Jeffol.RTM. A-480 as the catalyst. As another example, a ***thiol*** ester composition was reacted with methane diisocyanate at a stoichiometric value of 0.9 while using the DABCO catalyst.

DETD In the first MCO polythiourethane example, MCO was weighed into a polyethylene beaker. To the MCO agent was added Luprinate at a ***thiol*** to isocyanate mole ratio of 0.95. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick. The entire pre-polymer mixture was then poured into a mold for curing and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer.

DETD In the second MCO polythiourethane example, MCO was weighed into a polyethylene beaker. To the MCO agent was added Luprinate M20S at a ***thiol*** to isocyanate mole ratio of 1.00. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick. The entire pre-polymer mixture was then poured into a mold for curing and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer.

DETD In the polythiourethane compositions, the feedstock ***thiol*** ester compositions that were used included MSO (mercaptanized soybean oil), MHSO (mercaptohydroxy soybean oil), CMSO (cross-linked mercaptanized soybean oil), castor oil, and MCO (mercaptanized castor oil). The diisocyanates that were used to produce these compositions included MDI (4,4'-methylenebis(phenyl) diisocyanate), HMDI (4,4'-methylenebis(cyclohexyl) diisocyanate, which is also known as

hydrogenated MDI), TDI (tolylene 2,4-diisocyanate), HDI (1,6-diisocyanatohexane, which is also known as hexamethylene diisocyanate), and Luprinate.TM. M20S (which is an oligomerized form of MDI and is also referred to as polymeric MDI that is produced by BASF Corporation). The catalysts that were used included DABCO (diazabicyclooctane--di-tertiary amine), DBTDL (dibutyl tin dilaurate--organometallic catalyst), Jeffol.RTM.t A-480 (which is a tertiary amine polyol produced by Huntsman Based Chemicals), and BDMA (benzyldimethylamine).

DETD In the Fertilizer Examples, the following materials were used:

- A: Fertilizer particles--granular fertilizer grade urea, SGN 250, commercially available from Agrium;
- B1: Mercaptanized soybean oil (an example of MVO discussed above)--Polymercaptan 358, available from Chevron Phillips Chemical Co.; 8.65% ***thiol*** sulfur; 370 equivalent weight; viscosity of 510.6 cSt @ 21.degree. C.;
- B2: Mercapto-hydroxy soybean oil (an examples of MHVO discussed above)--A mercapto-hydroxy soybean oil made by the free radical addition of hydrogen sulfide to epoxidized soybean oil; the mercapto and hydroxy functionalities are equal; 8.335% ***thiol*** sulfur; equivalent weight 192 (including both mercapto and hydroxy functionalities);
- B3: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil made by the addition of elemental sulfur to mercaptanized soybean oil; ***thiol*** sulfur content 6.33%; equivalent weight 506;
- B4: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil made by the addition of elemental sulfur to mercaptanized soybean oil; ***thiol*** sulfur content 7.64%; equivalent weight 419; cross-linkcross-link
- C1: Isocyanate #17--A polymeric MDI, commercially available from BASF Canada, equivalent weight of 133;
- C2: Epoxy resin--5 minute epoxy resin, commercially available from ITW Devcon, Danvers, Mass. 01923 USA, equivalent weight 198;
- D1: Organic additive--Gulftene C30-HA alpha olefin wax, commercially available from Chevron Phillips Chemical Co., melting point 65.degree. C.--80.degree. C.;
- D2: Organic additive--Calwax 170, a microcrystalline wax commercially available from Calwax Corporation;
- E: Cross-linking agent--Jeffol A480, commercially available from Huntsman Polyurethanes; equivalent weight of 120; functionality 4.0; viscosity of 4000 cPs @25 C;

F1: Amine catalyst: Exp-9, commercially available from Huntsman Polyurethanes;
and
F2: Amine catalyst: 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU), CAS# ***6674-22-2***.

DETD Analysis of the ***Thiol*** Containing Esters, Hydroxy
Thiol Containing Esters and Cross-Linked ***Thiol***
Containing Ester

DETD Particular aspects of the ***thiol*** containing esters,
hydroxy
thiol containing esters, cross-linked ***thiol***
ester,
unsaturated esters and epoxidized unsaturated esters are measured
particular analytical techniques. ***Thiol*** sulfur values
were
obtained using a silver nitrate titration as described in ASTM
D3227 or
by Raman spectroscopy. Carbon-carbon double bond to ***thiol***
group molar ratio, cyclic sulfide to ***thiol*** group molar
ratios
were determined by ¹³C NMR and/or GC analysis of the
thiol
containing ester or hydroxy ***thiol*** containing ester side
chains.

DETD ***Thiol*** Sulfur Content by Raman Spectroscopy
DETD ***Thiol*** sulfur content was measured by both silver
nitrate
titration, ASTM D3227, and/or Raman spectroscopy. The Raman
spectroscopy
method is practiced by measuring the Raman spectra of the
thiol
containing ester, hydroxy ***thiol*** containing ester,
cross-linked
thiol ester and comparing the spectra to calibration
standards
containing know ***thiol*** compounds having know amounts of
thiol groups. Generally, the calibration standard
thiol
compound has a similar structure to the ***thiol***
containing
esters analyzed.

DETD The ***thiol*** containing esters, hydroxy ***thiol***
containing esters and cross-linked ***thiol*** ester
thiol
content were determined by comparing the Raman spectra of the
thiol containing esters, hydroxy ***thiol***
containing
esters and cross-linked ***thiol*** ester to calibration
standards
prepared from mercaptanized methyl oleate diluted in soybean oil
to
known ***thiol*** sulfur contents. ***Thiol*** sulfur
calibration standards were prepared using standards using various
known
concentration of mercaptanized methyl oleate diluted in soybean
oil.

DETD Raman spectra of the calibration standards and the ***thiol***
containing esters, hydroxy ***thiol*** containing esters and
cross-linked ***thiol*** ester were measured using a Kaiser
Hololab

5000 Process Raman spectrometer, using a 785 nm laser.

Thiol
 containing esters, hydroxy ***thiol*** containing esters and
 cross-linked ***thiol*** ester samples and the ***thiol***
 sulfur calibration standard Raman spectra were obtained by
 collecting
 four 10 second scans which were then processed using Holoreact
 software.

Thiol sulfur values for the ***thiol*** containing
 esters,
 hydroxy ***thiol*** containing esters and cross-linked
 thiol
 ester were then calculated using the ratio of the peak area
 values of
 the ***thiol*** SH peak (center: 2575 cm⁻¹; area 2500-2650
 cm⁻¹),
 and the C.dbd.O peak (center--1745 cm⁻¹; area--1700-1800 cm⁻¹)
 and
 comparing them to the peak area values for the calibration
 standards and
 interpolating the containing esters, hydroxy ***thiol***
 containing
 esters and cross-linked ***thiol*** ester ***thiol***
 sulfur
 contents. Repeatability of the ***thiol*** sulfur values as
 measured
 by Raman spectroscopy have been shown to have a standard
 deviation of
 0.05-0.1 and a % RSD of 0.6-1.5 using 5 samples having a %
 thiol
 sulfur content ranging from 3.1-10.6 weight percent as measured
 over a
 two month period.

DETD The Raman spectroscopy technique for determining the
 thiol
 sulfur content of a ***thiol*** containing ester, hydroxy
 thiol containing ester, and a cross-linked
 thiol
 containing ester has been illustrated using a ***thiol***
 containing
 ester produced from soybean oil. However, one skilled in the art
 may
 adapt and apply the Raman spectroscopy technique for determining
 the
 thiol sulfur content of other ***thiol***
 containing esters,
 hydroxy ***thiol*** containing esters, and a cross-linked
 thiol containing esters described herein.

DETD C.dbd.C to ***Thiol*** Group and Cyclic Sulfide Group to
 Thiol Group Molar Ratios by .sup.13C NMR

DETD Carbon-carbon double bond to ***thiol*** group molar ratio
 and
 cyclic sulfide group to ***thiol*** group molar ratios were
 determined by .sup.13C NMR. ***Thiol*** containing ester
 .sup.13C
 NMR spectra were obtained on a Varian Mercury INOVA400 NMR, a
 Varian
 Mercury Plus 300 NMR, or equivalent spectrometer (75.5 MHz
 .sup.13C
 NMR). Peak areas were determined for the cyclic sulfide carbon

atoms,
 thiol group HS--C carbon atoms and carbon-carbon double
 bonds
 carbon atoms using the .sup.13C NMR regions indicated in the
 table
 below:

Functional Group	.sup.13C NMR Region	Number of Carbon Atoms/Group
Cyclic Sulfide Carbon Atoms	49-49.5 ppm	2
HS--C Carbon Atoms	40-41.5 ppm	1
C.dbd.C Carbon Atoms	120-140 ppm	2

DETD The ***thiol*** containing ester cyclic sulfide to
 thiol
 group molar ratio were calculated by dividing the cyclic sulfide
 carbon
 atoms .sup.13C NMR peak area by 2 (to account for the 2 carbon
 atoms per
 cyclic sulfide group) and dividing the resultant number by the
 thiol group HS--C carbon atoms .sup.13C NMR peak area.
 The
 thiol containing ester carbon-carbon double bond to
 thiol group molar ratio were calculated by dividing the
 C.dbd.C
 carbon atoms .sup.13C NMR peak area by 2 (to account for the 2
 carbon
 atoms per carbon-carbon double bond) and dividing the result
 number by
 the ***thiol*** group HS--C carbon atoms .sup.13C NMR peak
 area
 Offset sample .sup.13C NMR's for soybean oil and a ***thiol***
 containing ester produced from soybean oil using the disclosed
 process
 is provided as FIG. 1.
 DETD The NMR technique for analyzing the unsaturated ester and the
 thiol containing ester produced from an unsaturated
 ester have
 been illustrated using .sup.13C NMR on soybean oil the
 thiol
 containing ester produced from soybean oil. However, one skilled
 in the
 art may adapt and apply either the .sup.13C NMR or .sup.1H NMR
 technique
 to analyze the unsaturated esters and ***thiol*** containing
 ester
 produced from the unsaturated ester described herein.
 DETD ***Epoxide*** Group to ***Thiol*** Group Molar Ratios by
 .sup.13C or .sup.1H NMR
 DETD The ***epoxide*** group to ***thiol*** group molar
 ratios were
 determined using .sup.1H or .sup.13C NMR. Hydroxy ***thiol***
 containing ester .sup.1H or .sup.13C NMR spectra were obtained on
 a
 Varian Mercury INOVA400 NMR, a Varian Mercury Plus 300 NMR, or
 equivalent spectrometer (300 MHz .sup.1H NMR-75.5 MHz .sup.13C
 NMR).
 Peak areas were determined for the ***epoxide*** group and
 sulfide

group using the .sup.13C and or .sup.1H regions indicated in the table below:

Functional Group	.sup.1H NMR Region	.sup.13C NMR Region	Number of Carbon Atoms/Group	Number of Hydrogen Atoms/Group
Epoxide	Group 2.75-3.2 ppm	53.6-56.6 ppm	2	2
Carbon Atoms				
HS--C Carbon Atoms	3.2-4 ppm	40-41.5 ppm	1	1
DETD The hydroxy group to	***thiol***	containing ester	***epoxide***	
thiol group molar ratio were calculated by dividing the ***epoxide*** group carbon atoms .sup.1H NMR peak area by 2 (to account for the 2 hydrogen atoms attached to the ***epoxide*** group carbon atoms) and dividing the result number by the ***thiol*** group HS--C carbon atom hydrogens IC NMR peak area. Similarly, the hydroxy ***thiol*** containing ester ***epoxide*** group to ***thiol*** group molar ratio were calculated using 13H NMR peak areas. DETD The average number of ***epoxide*** group per epoxidized unsaturated ester molecule can be determined utilizing similar methods utilizing either the carbonyl group carbon atom or the C--O ester group carbon atoms .sup.13C NMR peak areas in conjunction with the ***epoxide*** group .sup.13C NMR peak area. Sample .sup.1H NMR's epoxidized soybean oil and a ***thiol*** containing ester produced from epoxidized soybean oil 1 are provided in FIG. 2. DETD The NMR technique for analyzing the epoxidized unsaturated ester and the ***thiol*** containing ester produced from an epoxidized unsaturated ester (a hydroxy ***thiol*** containing ester) has been illustrated using .sup.1H NMR on epoxidized soybean oil the ***thiol*** containing ester produced from epoxidized soybean oil. However, one skilled in the art may adapt and apply either the .sup.1H NMR or .sup.13C NMR technique to analyze the epoxidized unsaturated esters and ***thiol*** containing ester produced from the epoxidized unsaturated ester described herein. DETD Analysis of Unsaturated Esters, Epoxidized Unsaturated Esters, ***Thiol*** Containing Esters, and Hydroxy ***Thiol*** Containing Esters by Methanolysis				

DETD Many properties of the unsaturated esters, epoxidized
 unsaturated esters, ***thiol*** containing esters, and hydroxy
 thiol containing ester were and/or can be determined by converting the
 complex ester molecules into their component polyols and carboxylic acid
 methyl esters. The converted esters are then analyzed by gas
 chromatography (GC) and/or gas chromatography/mass spectrometry (GCMS) to
 determine the composition of the complex ester side chains. Properties that are
 or can be determined by the methanolysis followed by GC or GC/MS of the
 carboxylic acid methyl esters include the number of side chain
 that contain ***thiol*** groups, the percent of ***thiol***
 group sulfur, the number of (or average number) of double bonds per
 ester molecule, the molecular weight distribution (or average molecular
 weight) of the ester side chains, the number of (or average
 number of) ***epoxide*** groups per ester molecule, the cyclic sulfide
 to ***thiol*** group molar ratio, the carbon-carbon double bond
 to ***thiol*** group molar ratio, and the ***epoxide***
 group to ***thiol*** group molar ratio, among others.

DETD Depending upon the material being subjected to the methanolysis
 procedure, there are two methanolysis procedures that were
 practiced upon the unsaturated ester, epoxidized esters, ***thiol***
 containing ester, and hydroxy ***thiol*** containing esters
 described within the experimental section.

DETD Unsaturated esters and ***thiol*** containing ester produced
 from unsaturated ester were subjected to a hydrogen chloride based
 methanolysis procedure. In the hydrogen chloride methanolysis
 procedure, a 50 to 100 mg sample of the ***thiol*** containing ester is
 contacted with 3 mL of 3 N methanolic HCl and reacted for 2 hours
 a 50.degree. C. The solution is then allowed to cool and the
 neutralized with a dilute sodium bicarbonate solution. The solution's organic
 components are then extracted with ethyl ether and analyzed by GC
 and/or GC/MS. Additional details for the methanolic hydrogen chloride
 methanolysis procedure may be found in the product specification
 sheet for methanolic HCl, 0.5 N and 3 N as supplied by Supelco.

DETD Epoxidized unsaturated esters and hydroxy ***thiol***
 containing esters produced from epoxidized unsaturated esters were subjected
 to a sodium methoxide based methanolysis procedure. The sodium
 methoxide

methanolysis procedure was based upon the procedure disclosed in U.S. Pat. No. 3,991,089. In the sodium methoxide methanolysis procedure, approximately 1 g of the ester was placed in a 50 mL vial with 5.0 mL 25% sodium methoxide in methanol, and 10 mL methanol. The mixture was shaken for approximately 1 hour at room temperature, during which time the solution became one phase. The mixture was then poured into 25 mL of distilled water. Diethyl ether, 25 mL, was added to the solution and the mixture was acidified with 0.5 N HCL to a pH of approximately 5. The organic layer was separated from the aqueous layer using a separatory funnel. The organic layer was washed successively with distilled water (15 mL) and brine solution (15 mL) and then dried over magnesium sulfate. The magnesium sulfate was separated from the organic solution by filtration and the solvent removed by rotary evaporation. DETD FIG. 3 provides a GC/MS trace of a mercaptanized soybean oil subjected to the methanolysis procedure and analyzed by GC/MS using a HP-5 30 m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column. Table 11 provides the GC/MS trace peak assignments. TABLE 11

GC/MS Data for Methanolysis of A ***Thiol*** Containing
Ester Produced from Soybean Oil
GC Retention time Methyl Ester Carboxylic Acid Assignment

21.58	Methyl hexadecanoate
23.66	Methyl (C18 monoene)oate
23.74	Methyl (C18 monoene)oate
23.96	Methyl octadecanoate
26.46	Methyl (C18 Monoene monomercaptan)oate
26.59	Methyl (C18 Monoene monomercaptan)oate
26.66	Methyl (C18 Monoene monomercaptan)oate
26.80	Methyl (C18 monomercaptan)oate
27.31	Methyl (C18 cyclic sulfide)oate
27.44	Methyl (C18 cyclic sulfide)oate
29.04	Methyl (C18 dimercaptan)oate
29.15	Methyl (C18 dimercaptan)oate
29.37	Methyl (C18 monoene dimercaptan)oate
29.46	Methyl (C18 monoene dimercaptan)oate
30.50	Methyl (C18 di (cyclic sulfide))oate

Peaks at 29.37 or 29.46 could also contain Methyl (C18 cyclic sulfide monomercaptan)oate isomers as part of those peaks.

DETD FIG. 5 provides a GC/MS trace of an epoxidized soybean oil contacted with hydrogen sulfide (a hydroxy ***thiol*** containing ester)

subjected to the methanolysis procedure and analyzed by GC/MS using a HP-5 30 m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column.

Table 13 provides the GC/MS trace peak assignments.

TABLE 13

GC/MS Data for Methanolysis of a Hydroxy ***Thiol*** Containing Ester Produced from Epoxidized Soybean Oil

GC Retention time Methyl Ester Carboxylic Acid Assignment

16.09	Methyl hexadecanoate
17.68	Methyl octadecanoate
18.94	Methyl (C18 monoepoxide)oate
19.94	Methyl (C18 diepoxide)oate
20.14	Methyl (C18 diepoxide)oate
20.75	Methyl (C18 monohydroxy monothiol)oate
21-21.5	Methyl (C18 triepoxide)oate
22.82	Methyl (C18 dihydroxy dithiol)oate
22.90	Methyl (C18 monoepoxide monohydroxy monothiol)oate
27-27.5	Unidentified mixture of C18 sulfur containing methyl esters

DETD The methanolysis procedure and GC/MS procedure has been illustrate

using soybean oil, epoxidized soybean oil, and the ***thiol*** containing products derived from soybean oil and epoxidized soybean oil.

However, one skilled in the art can easily adapt the procedures to the

analysis of other unsaturated esters, epoxidized unsaturated ester, and

the ***thiol*** containing products derived from the unsaturated

esters and epoxidized unsaturated esters as described herein.

DETD The polythiourethane produced from the ***thiol*** containing

esters, hydroxy ***thiol*** containing esters, and cross linked

thiol containing ester were analyzed using ASTM E1545-95A and

E228-95 to provide the glass transition temperatures and the coefficients of thermal expansion. Shore hardness of the polythiourethanes were determined using ASTM D2240-02A. The polythiourethane were also subject to a subjective analysis

classifying

the polythiourethanes as hard, flexible, rubbery, rigid, tough, brittle,

and other characteristics.

CLM What is claimed is:

1. A ***thiol*** ester composition comprising ***thiol*** ester

molecules having an average of at least 1.5 ester groups per

thiol ester molecule, having an average of at least 1.5

thiol groups per ***thiol*** ester molecule, and

having a

molar ratio of cyclic sulfides to ***thiol*** groups of less

than

1.5.

CLM What is claimed is:
2. The ***thiol*** ester composition of claim 1, wherein the
 thiol ester molecules have a molar ratio of cyclic
sulfides to
 thiol groups ranging from 0 to 1.0.

CLM What is claimed is:
3. The ***thiol*** ester composition of claim 1, wherein the
 thiol ester molecules have an average ranging from 1.5
to 9
 thiol groups per ***thiol*** ester molecule.

CLM What is claimed is:
4. The ***thiol*** ester composition of claim 1, wherein the
 thiol ester molecules have a molar ratio of carbon-
carbon double
bonds to ***thiol*** groups of less than 1.5.

CLM What is claimed is:
5. The ***thiol*** ester composition of claim 1, wherein the
 thiol ester molecules have an average of greater than 2
weight
percent ***thiol*** sulfur.

CLM What is claimed is:
6. The ***thiol*** ester composition of claim 1, wherein
 thiol ester molecules have an average ranging from 8 to
10
weight percent ***thiol*** sulfur.

CLM What is claimed is:
7. The ***thiol*** ester composition of claim 1, wherein the
 thiol ester molecules have an average of less than 30
mole
percent total sulfur present as cyclic sulfides.

CLM What is claimed is:
8. The ***thiol*** ester composition of claim 1, wherein the
 thiol ester molecules have an average of less than 10
mole
percent total sulfur present as cyclic sulfides.

CLM What is claimed is:
9. The ***thiol*** ester composition of claim 1, wherein
greater
than 40 percent of ***thiol*** ester molecule total side
chains
contain sulfur.

CLM What is claimed is:
10. A process for producing a ***thiol*** ester composition
comprising the steps of: a) contacting hydrogen sulfide and an
unsaturated ester composition comprising unsaturated esters
having an
average of at least 1.5 ester groups per unsaturated ester
molecule and
having an average of at least 1.5 carbon-carbon double bonds per
unsaturated ester molecule; and b) reacting the hydrogen sulfide
and

the unsaturated esters to form a ***thiol*** ester composition comprising ***thiol*** ester molecules having a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

CLM What is claimed is:
15. The process of claim 10, wherein the ***thiol*** ester molecules have a molar ratio of the hydrogen sulfide to carbon-carbon double bonds of greater than 2.

CLM What is claimed is:
18. The process of claim 10, wherein the ***thiol*** ester molecules have an average of greater than 5 weight percent ***thiol*** sulfur.

CLM What is claimed is:
20. The process of claim 10, wherein greater than 40 percent of the ***thiol*** ester molecule total side chains contain sulfur.

CLM What is claimed is:
22. A process for producing a ***thiol*** ester composition comprising the steps of: a) contacting hydrogen sulfide and an unsaturated ester composition comprising unsaturated esters having an average of at least 1.5 ester groups per unsaturated ester molecule and having an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule; and b) reacting the hydrogen sulfide and the unsaturated esters in a substantial absence of a solvent to form the ***thiol*** ester composition comprising ***thiol*** ester molecules.

CLM What is claimed is:
25. The process of claim 22, wherein the ***thiol*** ester molecules have a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

CLM What is claimed is:
26. The process of claim 22, wherein the ***thiol*** ester molecules have a molar ratio of the hydrogen sulfide to carbon-carbon double bonds is greater than 1.

CLM What is claimed is:
29. The process of claim 22, wherein the ***thiol*** ester molecules have an average of greater than 5 weight percent ***thiol*** sulfur.

CLM What is claimed is:
31. The process of claim 22, wherein greater than 40 percent of
the ***thiol*** ester molecule total side chains contain sulfur.

CLM What is claimed is:
32. A process for preparing a ***thiol*** ester composition
comprising: a) contacting a polyol composition and a
thiol
carboxylic acid composition; and b) reacting the polyol
composition and
the ***thiol*** carboxylic acid composition to produce the
thiol ester composition comprising ***thiol***
ester
molecules having an average of at least 1.5 ester groups per
thiol ester molecule and having an average of at least
1.5
thiol groups per ***thiol*** ester molecule.

IT 102-85-2, Tri-n-butylphosphite ***6674-22-2*** ,
1,8-Diazabicyclo[5.4.0]undec-7-ene
(activator; thiol ester compns. prepd. by reacting H2S with
unsatd.
esters, such as soybean oil for manuf. monomers for prodn. of
polythiourethanes for fertilizers)

L7 ANSWER 31 OF 60 USPATFULL on STN
ACCESSION NUMBER: 2005:227538 USPATFULL <<LOGINID::20091205>>
TITLE: ***Thiol*** ester compositions and processes
for
making and using same
INVENTOR(S): Byers, Jim D., Bartlesville, OK, UNITED STATES
Refvik, Mitchell D., Bartlesville, OK, UNITED
STATES
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PATENT ASSIGNEE(S): Chevron Phillips Chemical Company LP (U.S.
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	NUMBER	KIND	DATE
PATENT INFORMATION:	US 20050197390	A1	20050908
APPLICATION INFO.:	US 2005-59792	A1	20050217 (11)

	NUMBER	DATE
PRIORITY INFORMATION:	US 2004-545260P	20040217 (60)
	US 2004-561614P	20040413 (60)
	US 2004-561685P	20040413 (60)
	US 2004-561855P	20040413 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION
LEGAL REPRESENTATIVE: CHEVRON PHILLIPS CHEMICAL COMPANY LP, LAW
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US
NUMBER OF CLAIMS: 18
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 14 Drawing Page(s)
LINE COUNT: 6310
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI ***Thiol*** ester compositions and processes for making and
 using
 same
 AB ***Thiol*** ester compositions, methods of making the
 thiol
 ester compositions, and methods of using the ***thiol***
 ester
 compositions are provided. In some embodiments, the ***thiol***
 ester compositions include ***thiol*** esters, hydroxy
 thiol
 esters and cross-linked ***thiol*** esters. The ***thiol***
 ester composition can be used to produce cross-linked
 thiol
 esters, sulfonic acid-containing esters, sulfonate containing
 esters and
 thioacrylate containing esters. The ***thiol*** ester
 compositions
 can be used to produce polythiourethanes. The polythiourethanes
 can be
 used in fertilizers and fertilizer coatings.
 SUMM The invention relates to ***thiol*** containing ester
 compositions
 generally made from a reaction of unsaturated ester compositions
 and a
 material capable of forming a ***thiol*** group. The
 invention also
 relates to the processes for preparing such ***thiol***
 containing
 compositions and uses for the ***thiol*** containing
 compositions.

SUMM The present invention advantageously provides ***thiol***
 containing compositions and methods of making such compositions.
 In
 addition to the compositions and methods of making such
 compositions,
 products that include such compositions are also provided.

SUMM As an embodiment of the present invention, a ***thiol***
 ester
 composition is advantageously provided. In this embodiment, the
 thiol ester composition includes ***thiol*** ester
 molecules
 that have an average of at least 1.5 ester groups per
 thiol
 ester molecule. The ***thiol*** ester molecules also have an
 average
 of at least 1.5 ***thiol*** groups per ***thiol*** ester
 molecule. The ***thiol*** ester molecules also have a molar
 ratio of
 cyclic sulfides to ***thiol*** groups of less than 1.5.

SUMM In some aspects, the ***thiol*** ester molecules have a
 molar ratio
 of cyclic sulfides to ***thiol*** groups ranging from 0 to
 1.0. In
 some aspects, the ***thiol*** ester molecules have an average
 ranging from 1.5 to 9 ***thiol*** groups per ***thiol***
 ester
 molecule. In some embodiments, the ***thiol*** ester

molecules have

a molar ratio of carbon-carbon double bonds to ***thiol*** groups of less than 1.5.

SUMM The amount of ***thiol*** sulfur or ***mercaptan*** sulfur contained within the ***thiol*** ester molecules can also vary. For example, in some embodiments, the ***thiol*** ester molecules have an average of greater than 5 weight percent ***thiol*** sulfur. In other embodiments, the ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur. In some embodiments, the ***thiol*** ester molecules have an average of less than 30 mole percent sulfur, which is present as cyclic sulfides. Alternatively, the ***thiol*** ester molecules have an average of less than 2 mole percent sulfur present as cyclic sulfides.

SUMM In some embodiments, the ***thiol*** ester molecules are produced from unsaturated esters that have an average of less than 25 weight percent of side chains that include 3 contiguous methylene interrupted carbon-carbon double bonds. In another aspect, greater than 40 percent of the total side chains contained within the ***thiol*** ester molecules contain sulfur.

SUMM In addition to the ***thiol*** ester composition, a process for producing the ***thiol*** ester composition is advantageously provided as another embodiment of the present invention. To produce the ***thiol*** ester composition, hydrogen sulfide is contacted with an unsaturated ester composition. The unsaturated ester composition includes unsaturated esters that have an average of at least 1.5 ester groups per unsaturated ester molecule. The unsaturated esters also have an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are reacted to produce or form the ***thiol*** ester composition. The ***thiol*** ester composition advantageously includes ***thiol*** ester molecules that have a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

SUMM Another process for producing the ***thiol*** ester

composition is advantageously provided as another embodiment of the present invention. In this process embodiment, the hydrogen sulfide and the unsaturated ester composition are contacted. The unsaturated ester composition includes unsaturated esters having an average of at least 1.5 ester groups per unsaturated ester molecule and having an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are then reacted in a substantial absence of a solvent to form the ***thiol*** ester composition. The ***thiol*** ester composition includes ***thiol*** ester molecules. The ***thiol*** ester composition advantageously includes ***thiol*** ester molecules that have a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

SUMM The resulting ***thiol*** ester molecules produced by this process possess advantageous characteristics. For example, in some embodiments, the ***thiol*** ester molecules have a molar ratio of the hydrogen sulfide to carbon-carbon double bonds of greater than 2. As another example, in other embodiments, the ***thiol*** ester molecules have an average of greater than 5 weight percent ***thiol*** sulfur. In some aspects, greater than 40 percent of the ***thiol*** ester molecule total side chains contain sulfur.

SUMM As another embodiment of the present invention, another process for preparing the ***thiol*** ester composition is advantageously provided. In this embodiment, a polyol composition and a ***thiol*** carboxylic acid composition are contacted and reacted to produce the ***thiol*** ester composition. The ***thiol*** ester composition includes ***thiol*** ester molecules having an average of at least 1.5 ester groups per ***thiol*** ester molecule and having an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule.

SUMM In addition to the ***thiol*** ester composition, other compositions are advantageously provided as embodiments of the present

invention. For example, a hydroxy ***thiol*** ester composition is provided as another embodiment of the present invention. The hydroxyl ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules having an average of at least 1.5 ester groups per hydroxy ***thiol*** ester molecule and having an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

SUMM As described herein, the .alpha.-hydroxy ***thiol*** groups contain an alcohol or hydroxy group and a ***thiol*** group within the same group. In embodiments of the present invention, the .alpha.-hydroxy ***thiol*** groups can be replaced with separate alcohol and ***thiol*** groups. In these embodiments, the same number of .alpha.-hydroxy groups can be used for the separate alcohol and ***thiol*** groups. For example, in some embodiments, the hydroxy ***thiol*** ester molecules have an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups. In embodiments that contain separate alcohol and ***thiol*** groups, the hydroxy ***thiol*** ester molecules would contain an average of at least 1.5 alcohol groups and an average of at least 1.5 ***thiol*** groups.

SUMM In some aspects, the hydroxy ***thiol*** ester molecules have an average ranging from 1.5 to 9 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule. In some embodiments, the ***thiol*** ester molecules have a molar ratio of carbon-carbon double bonds to ***thiol*** groups of less than 1.5.

SUMM In some embodiments, the ***thiol*** ester molecules are produced from unsaturated esters that have an average of less than 25 weight percent of side chains that include 3 contiguous methylene interrupted carbon-carbon double bonds. In another aspect, greater than 40 percent of the total side chains contained within the .alpha.-hydroxy ***thiol*** ester molecules contain sulfur.

SUMM The amount of ***thiol*** sulfur contained within the hydroxy ***thiol*** ester molecules can also vary. For example, in some embodiments, the hydroxy ***thiol*** ester molecules have an average

of greater than 5 weight percent ***thiol*** sulfur. In other embodiments, the hydroxy ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur.

SUMM In some embodiments, the hydroxy ***thiol*** ester molecules have a molar ratio of ***epoxide*** groups to the .alpha.-hydroxy ***thiol*** groups of less than 2. In other aspects, the composition is substantially free of ***epoxide*** groups.

SUMM In addition to the hydroxy ***thiol*** ester composition, methods or processes for making the hydroxy ***thiol*** ester composition are advantageously provided as embodiments of the present invention. In an embodiment, a process for preparing the hydroxy ***thiol*** ester composition is provided that includes the step of contacting the hydrogen sulfide and an epoxidized unsaturated ester composition. The epoxidized unsaturated ester composition includes epoxidized esters having an average of at least 1.5 ester groups per epoxidized unsaturated ester molecule and having an average of at least 1.5 ***epoxide*** groups per epoxidized unsaturated ester molecule. The hydrogen sulfide and the epoxidized unsaturated esters are then reacted to form the hydroxy ***thiol*** ester composition.

SUMM In some embodiments, a molar ratio of the hydrogen sulfide to ***epoxide*** groups in the epoxidized unsaturated esters is greater than 1.

SUMM Another process for preparing the hydroxy ***thiol*** ester composition is advantageously provided as another embodiment of the present invention. In this process embodiment, a polyol composition and a hydroxy ***thiol*** carboxylic acid composition are contacted and reacted to produce the hydroxy ***thiol*** ester composition. In this embodiment, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules having an average of at least 1.5 ester groups per hydroxy ***thiol*** ester molecule and having an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

SUMM A cross-linked ***thiol*** ester composition is advantageously

provided as another embodiment of the present invention. The cross-linked ***thiol*** ester composition includes

thiol ester oligomers having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1. In some embodiments, the ***thiol*** ester oligomers have at least three ***thiol*** ester monomers connected by polysulfide linkages. In another aspect, the ***thiol*** ester oligomers have from 3 to 20 ***thiol*** ester monomers connected by polysulfide linkages.

SUMM In an aspect, the cross-linked ***thiol*** ester composition includes both ***thiol*** ester monomers and ***thiol*** ester oligomers. In some embodiments, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total ***thiol*** sulfur content ranging from 0.5 to 8 weight percent; or alternatively, ranging from 8 to 15 weight percent. The combined ***thiol*** ester monomers and ***thiol*** ester oligomers can have an average molecular weight greater than 2000; or alternatively, in a range from 2000 to 20,000.

SUMM As another embodiment of the present invention, a cross-linked ***thiol*** ester composition produced by the process comprising the steps of contacting the ***thiol*** ester composition with an oxidizing agent and reacting the ***thiol*** ester and the oxidizing agent to form ***thiol*** ester oligomers is advantageously provided. In this embodiment, the ***thiol*** ester oligomers have at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1.

SUMM A process to produce the cross-linked ***thiol*** ester composition is also advantageously provided as another embodiment of the present invention. In this process, a ***thiol*** ester composition is contacted and reacted with an oxidizing agent to form ***thiol*** ester oligomers having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1. In some embodiments, the oxidizing agent is

elemental sulfur, oxygen, or hydrogen peroxide. In an aspect, the oxidizing agent is elemental sulfur.

SUMM In an aspect, the ***thiol*** ester is a hydroxy
thiol ester. In other aspects, a weight ratio of elemental sulfur to
thiol sulfur in the ***thiol*** ester molecules
ranges from
0.5 to 32.

SUMM The step of the reacting the ***thiol*** ester and the
oxidizing
agent can be performed at a temperature ranging from 25.degree.
C. to
150.degree. C. The process for producing the cross-linked
thiol
ester composition can also include the step of stripping residual
hydrogen sulfide from the cross-linked ***thiol*** ester
composition
produced. In another aspect, the reaction of the ***thiol***
ester
and the elemental sulfur is catalyzed. In some embodiments, the
catalyst
is an amine.

SUMM In another of its aspects, the present invention relates to a
controlled release fertilizer material comprising a particulate
plant
nutrient surrounded by a coating which is the reaction product of
a
mixture comprising: (i) a first component selected from an
isocyanate
and/or an epoxy resin, and (ii) a first active hydrogen-
containing
compound selected from the group consisting of a ***thiol***
ester
composition; a hydroxy ***thiol*** ester composition; a
cross-linked
thiol ester composition and mixtures thereof.

SUMM In another of its aspects, the present invention relates to a
process
for the production of abrasion resistant polythiourethane and/or
epoxy
polymer encapsulated controlled release fertilizer particles by
incorporating in urethane and/or epoxy polymer forming reaction
mixture
a sulfur-containing compound such as one or more of a
thiol
ester composition; a hydroxy ***thiol*** ester composition; a
cross-linked ***thiol*** ester composition, other sulfur-
based
compounds described herein below and mixtures thereof.

SUMM Preferably, for the production of the present polythiourethane
encapsulated controlled release fertilizer material, a sulfur-
containing
compound (e.g., one or more of a ***thiol*** ester
composition; a
hydroxy ***thiol*** ester composition; a cross-linked

thiol

ester composition) is used as one of the isocyanate-reactive components (alone or in combination with other active hydrogen-containing compounds). Preferably, the sulfur-containing compound comprises a sulfur-containing vegetable oil. In one preferred embodiment, the sulfur-containing vegetable oil comprises a mercaptanized vegetable oil (MVO), more preferably as described in more detail herein, even more preferably an MVO produced by the addition of hydrogen sulfide to a vegetable oil. In another preferred embodiment, the sulfur-containing vegetable oil comprises mercapto-hydroxy vegetable oil (MHVO), more preferably as described in more detail herein, even more preferably an MHVO produced by the addition of hydrogen sulfide to epoxidized vegetable oil. In yet another preferred embodiment, the sulfur-containing vegetable oil comprises sulfur cross-linked mercaptanized vegetable oil (CMVO), more preferably as described in more detail herein, even more preferably an CMVO produced by the addition of elemental sulfur to mercaptanized vegetable oil (MVO).

SUMM Preferably, for the production of epoxy polymer encapsulated controlled release fertilizer material, a sulfur-containing compound (e.g., one or more of a ***thiol*** ester composition; a hydroxy ***thiol*** ester composition; a cross-linked ***thiol*** ester composition) is used as one of the isocyanate-reactive components (alone or in combination with other active hydrogen-containing compounds). Preferably, the sulfur-containing compound comprises a sulfur-containing vegetable oil (e.g., MVO and/or MHVO and/or CMVO) is used as one of the epoxy resin-reactive components.

DRWD FIG. 1 includes two graphs that compare the NMR's of soybean oil, which is shown in the top graph, and a ***thiol*** containing ester produced from soybean oil in accordance with an embodiment of the present invention, which is shown in the bottom graph;

DRWD FIG. 2 includes two graphs that compare the NMR's of epoxidized soybean oil, which is shown in the top graph, and a ***thiol*** containing ester produced from epoxidized soybean oil in accordance with an embodiment of the present invention, which is shown in the bottom graph;

DRWD FIG. 3 is a gas chromatograph (GC)/mass spectrometer (MS) trace of a ***thiol*** containing ester that was produced from soybean oil in accordance with an embodiment of the present invention and then

treated
by methanolysis;
DRWD FIG. 5 is a GC/MS trace of hydroxy ***thiol*** containing
ester
produced from epoxidized soybean oil in accordance with an
embodiment of
the present invention and then treated by methanolysis;
DETD In this specification, " ***thiol*** ester composition"
refers to an
ester composition that includes " ***thiol*** ester
molecules." The
thiol ester molecule has at least one ***thiol***
group and
at least one ester group within the ***thiol*** ester
molecule.
DETD In this specification, "hydroxy ***thiol*** ester
composition"
refers to an ester composition that includes "hydroxy
thiol
ester molecules." The hydroxy ***thiol*** ester molecule has
at
least one ***thiol*** group, at least one ester group, and at
least
one hydroxy or alcohol group within the hydroxy ***thiol***
ester
molecule. Alternatively, the alcohol group and the ***thiol***
group
can be combined in the same group, which is referred to as an
".alpha.-hydroxy ***thiol*** group."
DETD In this specification, "polythiourethane" refers to a urethane
composition that includes more than one of the following
structure:
##STR1## The presence of the thiourethane group can be
determined by
method known to those skilled in the art (for example infrared
spectroscopy, Raman spectroscopy, and/or NMR). ***Thiol***
Ester
Composition
DETD The present invention advantageously provides a ***thiol***
ester
composition as an embodiment of the present invention. The
thiol
ester composition includes ***thiol*** ester molecules that
have an
average of at least 1.5 ester groups and an average of at least
1.5
thiol groups per ***thiol*** ester molecule. The
thiol ester composition also has a molar ratio of
cyclic
sulfides to ***thiol*** groups of less than 1.5, as described
herein.
DETD Generally, the ***thiol*** ester composition contains
molecules
having at least one ester group and at least one ***thiol***
group.
The ***thiol*** ester composition of this invention can be
produced
from any unsaturated ester, as described herein. Because the
feedstock
unsaturated esters can contain multiple carbon-carbon double

bonds per unsaturated ester molecule, carbon-carbon double bond reactivity and statistical probability dictate that each ***thiol*** ester molecule of the ***thiol*** ester composition produced from the unsaturated ester composition will not have the same number of ***thiol*** groups, number of unreacted carbon-carbon double bonds, number of cyclic sulfides, molar ratio of carbon-carbon double bonds to ***thiol*** groups, molar ratio of cyclic sulfides to ***thiol*** groups and other quantities of functional groups and molar ratios disclosed herein as the feedstock unsaturated ester. Additionally, the feedstock unsaturated esters can also comprise a mixture of individual esters having a different number of carbon-carbon double bonds and/or ester groups. Thus, many of these properties will be discussed as an average number of the groups per ***thiol*** ester molecule within the ***thiol*** ester composition or average ratio per ***thiol*** ester molecule within the ***thiol*** ester composition. In other embodiments, it is desired to control the content of ***thiol*** sulfur present in the ***thiol*** ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every carbon-carbon double bond within the unsaturated ester, certain molecules of ***thiol*** ester can have more or less ***thiol*** groups than other molecules. Thus, the weight percent of ***thiol*** groups is stated as an average across all ***thiol*** ester molecules of the ***thiol*** ester composition.

DETD The ***thiol*** ester can be derived from any unsaturated ester described herein.

DETD The ***thiol*** ester compositions can be described as comprising one or more separate or discreet functional groups of the ***thiol*** ester molecule and/or ***thiol*** ester composition. These independent functional groups can include: the number of (or average number of) ester groups per ***thiol*** ester molecule, ***thiol*** containing the number of (or average number of) ***thiol*** groups per ***thiol*** ester molecule, the number of (or average number of) unreacted carbon-carbon double bonds per ***thiol*** ester molecule, the average ***thiol***

sulfur content of the ***thiol*** ester composition, the percentage (or average percentage) of sulfide linkages per ***thiol*** ester molecule, and the percentage (or average percentage) of cyclic sulfide groups per ***thiol*** ester molecule. Additionally, the ***thiol*** ester compositions can be described using individual or a combination of ratios including the ratio of double bonds to ***thiol*** groups, the ratio of cyclic sulfides to ***mercaptan*** group, and the like.

As separate elements, these functional groups of the ***thiol*** composition will be described separately.

DETD Minimally, in some embodiments, the ***thiol*** ester contains ***thiol*** ester molecules having at least one ester group and one ***thiol*** group per ***thiol*** ester molecule. As the ***thiol*** ester is prepared from unsaturated esters, the ***thiol*** ester can contain the same number of ester groups as the unsaturated esters described herein. In an embodiment, the ***thiol*** ester molecules have an average of at least 1.5 ester groups per ***thiol*** ester molecule. Alternatively, the ***thiol*** ester molecules have an average of at least 2 ester groups per ***thiol*** ester molecule; alternatively, an average of at least 2.5 ester groups per ***thiol*** ester molecule; or alternatively, an average of at least 3 ester groups per ***thiol*** ester molecule. In other embodiments, the ***thiol*** esters have an average of from 1.5 to 8 ester groups per ***thiol*** ester molecule; alternatively, an average of from 2 to 7 ester groups per ***thiol*** ester molecule; alternatively, an average of from 2.5 to 5 ester groups per ***thiol*** ester molecule; or alternatively, an average of from 3 to 4 ester groups per ***thiol*** ester molecule. In yet other embodiments, the ***thiol*** ester comprises an average of 3 ester groups per ***thiol*** ester molecule or alternatively, an average of 4 ester groups per unsaturated ester molecule.

DETD Minimally, the ***thiol*** ester comprises an average of at least one ***thiol*** group per ***thiol*** ester molecule. In an embodiment, the ***thiol*** ester molecules have an average of at least 1.5 ***thiol*** groups per ***thiol*** ester

molecule;
alternatively, ***thiol*** containing an average of at least
2
thiol groups per ***thiol*** ester molecule;
alternatively,
an average of at least 2.5 ***thiol*** groups per
thiol
ester molecule; or alternatively, an average of at least 3
thiol
groups per ***thiol*** ester molecule. In other embodiments,
the
thiol ester molecules have an average of from 1.5 to 9
thiol groups per ***thiol*** ester molecule;
alternatively,
an average of from 3 to 8 ***thiol*** groups per
thiol
ester molecule; alternatively, ***thiol*** containing an
average of
from 2 to 4 ***thiol*** groups per ***thiol*** ester
molecule,
or alternatively, an average of from 4 to 8 ***thiol***
groups per
thiol ester molecule.
DETD In other embodiments, the ***thiol*** ester can be described
by the
average amount of ***thiol*** sulfur present in ***thiol***
ester. In an embodiment, the ***thiol*** ester molecules have
an
average of at least 5 weight percent ***thiol*** sulfur per
thiol ester molecule; alternatively, an average of at
least 10
weight percent ***thiol*** sulfur per ***thiol*** ester
molecule, or alternatively, an average of greater than 15 weight
percent
thiol sulfur per ***thiol*** ester molecule. In an
embodiment, the ***thiol*** ester molecules have an average
of from
5 to 25 weight percent ***thiol*** sulfur per ***thiol***
ester
molecule; alternatively, an average of from 5 to 20 weight
percent
thiol sulfur per ***thiol*** ester molecule;
alternatively,
an average of from 6 to 15 weight percent ***thiol*** sulfur
per
thiol ester molecule; or alternatively, an average of
from 8 to
10 weight percent ***thiol*** sulfur per ***thiol***
ester
molecule.
DETD Generally, the location of the ***thiol*** group of the
thiol ester is not particularly important and will be
dictated
by the method used to produce the ***thiol*** ester. In
embodiments
wherein the ***thiol*** ester is produced by contacting an
unsaturated ester, the position of the ***thiol*** group will
be
dictated by the position of the carbon-carbon double bond. When
the

carbon-carbon double bond is an internal carbon-carbon double bond, the method of producing the ***thiol*** ester will result in a secondary ***thiol*** group. However, when the double bond is located at a terminal position it is possible to choose reaction conditions to produce a ***thiol*** ester comprising either a primary ***thiol*** group or a secondary ***thiol*** group.

DETD Some methods of producing the ***thiol*** ester composition can additionally create sulfur containing functional groups other than a ***thiol*** group. For example, in some ***thiol*** ester production methods, an introduced ***thiol*** group can react with a carbon-carbon double bond within the same unsaturated ester to produce a sulfide linkage. When the reaction is with a double bond of a second unsaturated ester, this produces a simple sulfide linkage.

However, in some instances, the second carbon-carbon double bond is located in the same unsaturated ester molecule. When the ***thiol*** group reacts with a second carbon-carbon double bond within the same unsaturated ester molecule, a sulfide linkage is produced. In some instances, the carbon-carbon double bond can be within a second ester group of the unsaturated ester molecule. While in other instances, the carbon-carbon double bond can be within the same ester group of the unsaturated ester molecule.

DETD When the ***thiol*** group reacts with the carbon-carbon double bond in a second ester group of the same unsaturated ester molecule, the cyclic sulfide would contain two ester groups contained within a ring structure. When the ***thiol*** group reacts with the carbon-carbon double bond within the same ester group, the cyclic sulfide would not contain an ester group within the ring structure. Within this specification, this second type of cyclic sulfide is referred to as a cyclic sulfide. Within this specification, the first type of cyclic sulfide is referred to as a simple sulfide. In the cyclic sulfide case, the sulfide linkage produces a cyclic sulfide functionality within a single ester group of the ***thiol*** ester. This linkage is termed a cyclic sulfide for purposes of this application. One such sulfide

group that can be produced is a cyclic sulfide. The cyclic sulfide rings that can be produced include a tetrahydrothiopyran ring, a thietane ring, or a thiophane ring (tetrahydrothiophene ring).

DETD In some embodiments, it is desirable to control the average amount of sulfur present as cyclic sulfide in the ***thiol*** ester. In an embodiment the average amount of sulfur present as cyclic sulfide in the ***thiol*** ester molecules comprises less than 30 mole percent.

Alternatively, the average amount of sulfur present as cyclic sulfide in the ***thiol*** esters comprises less than 20 mole percent; alternatively, less than 10 mole percent; alternatively, less than 5 mole percent; or alternatively, less than 2 mole percent. In other embodiments, it is desired to control the molar ratio of cyclic sulfides to ***thiol*** groups. In other embodiments, it is desirable to have molar ratios of cyclic sulfide to ***thiol*** group. In an embodiment, the average molar ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester is less than 1.5. Alternatively, the average molar ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester is less than 1; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, 0.1. In some embodiments, the ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester ranges from 0 to 1; or alternatively, the average molar ratio of cyclic sulfide groups to ***thiol*** group per ***thiol*** ester ranges between 0.05 and 1.

DETD In some instances it can be desirable to have carbon-carbon double bonds present in the ***thiol*** ester composition while in other embodiments it can be desirable to minimize the number of carbon-carbon double bonds present in the ***thiol*** ester composition.

The presence of carbon-carbon double bonds present in the ***thiol*** ester can be stated as an average molar ratio of carbon-carbon double bonds to ***thiol*** -sulfur. In an embodiment, the average ratio of the remaining unreacted carbon-carbon double bond in the ***thiol*** ester composition to ***thiol*** sulfur is less than 1.5 per ***thiol*** ester molecule. Alternatively, the average ratio of carbon-carbon double bond to ***thiol*** sulfur is less than 1.2 per

thiol ester molecule; alternatively, less than 1.0 per
 thiol ester molecule; alternatively, less than 0.75 per
 thiol ester molecule; alternatively, less than 0.5 per
 thiol ester molecule; alternatively, less than 0.2 per
 thiol ester molecule; or alternatively, less than 0.1

per

thiol ester molecule.
 DETD In particular embodiments, the ***thiol*** ester is produced
 from unsaturated ester compositions. Because the feedstock unsaturated
 ester has particular compositions having a certain number of ester
 groups present, the product ***thiol*** ester composition will have
 about the same number of ester groups per ***thiol*** ester
 molecule as the feedstock unsaturated ester. Other, independent ***thiol***
 ester properties described herein can be used to further describe
 the ***thiol*** ester composition.

DETD In some embodiments, the ***thiol*** ester molecules are
 produced from unsaturated esters having an average of less than 25 weight
 percent of side chains having 3 contiguous methylene interrupted carbon-
 carbon double bonds, as described herein. In some embodiments, greater
 than 40 percent of the ***thiol*** containing natural source total
 side chains can include sulfur. In some embodiments, greater than 60
 percent of the ***thiol*** ester molecule total side chains can
 include sulfur. In other embodiments, greater than 50, 70, or 80 percent
 of the ***thiol*** ester molecule total side chains can include
 sulfur.

DETD In an embodiment, the ***thiol*** ester is a ***thiol***
 containing natural source oil, as described herein. When the
 thiol ester is a ***thiol*** containing natural
 source oil, functional groups that are present in the ***thiol***
 containing natural source oil can be described in a "per ***thiol***
 ester molecule" basis or in a "per triglyceride" basis. The
 thiol containing natural source oil can have substantially the same
 properties as the ***thiol*** ester composition, such as the molar
 ratios and other independent descriptive elements described herein.

DETD The average number of ***thiol*** groups per triglyceride in
 the ***thiol*** containing natural source oil is greater than
 about 1.5.

In some embodiments, the average number of ***thiol*** groups
 per

triglyceride can range from about 1.5 to about 9.

DETD The ***thiol*** ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an unsaturated ester composition and can be further limited by the process as described herein. The ***thiol*** containing natural source oil can also be described using a molecular weight or an average molecular weight of the side chains.

DETD Hydroxy ***Thiol*** Ester Composition

DETD In embodiments of the present invention, the ***thiol*** ester compositions can also contain a hydroxy or alcohol group. When the ***thiol*** ester composition includes the hydroxy group, the ***thiol*** ester composition is referred to herein as the hydroxy ***thiol*** ester composition. The quantity or number of alcohol groups present in the hydroxy ***thiol*** ester composition can be independent of the quantity of other functional groups present in the hydroxy ***thiol*** ester composition (i.e. ***thiol*** ester groups, sulfides, cyclic sulfides). Additionally, the weight percent of ***thiol*** sulfur and functional group ratios (i.e. molar ratio of cyclic sulfides to ***thiol*** groups, molar ratio of ***epoxide*** groups to ***thiol*** groups, molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups and other disclosed quantities of functional groups and their molar ratios to the ***thiol*** groups) are separate or discreet elements that can be used to describe the hydroxy ***thiol*** ester composition.

The hydroxy ***thiol*** ester composition can be described using any combination of the hydroxy ***thiol*** ester composition separate functional groups or ratios described herein.

DETD In an embodiment, the hydroxy ***thiol*** ester composition is produced by reacting hydrogen sulfide with an epoxidized unsaturated ester composition as described herein. Because the epoxidized unsaturated ester can contain multiple ***epoxide*** groups, ***epoxide*** group reactivity and statistical probability dictate that not all hydroxy ***thiol*** ester molecules of the hydroxy ***thiol*** ester composition will have the same number of

hydroxy groups, ***thiol*** groups, .alpha.-hydroxy ***thiol*** groups, sulfides, cyclic sulfides, molar ratio of cyclic sulfides to ***thiol*** groups, molar ratio of ***epoxide*** groups to ***thiol*** groups, molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups, weight percent ***thiol*** sulfur and other disclosed quantities of functional groups and their molar ratios as the epoxidized unsaturated ester composition. Thus, many of these properties will be discussed as an average number or ratio per hydroxy ***thiol*** ester molecule. In other embodiments, it is desired to control the content of ***thiol*** sulfur present in the hydroxy ***thiol*** ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every ***epoxide*** group within the epoxidized unsaturated ester, certain hydroxy ***thiol*** ester molecules can have more or less ***thiol*** groups than other molecules within the hydroxy ***thiol*** ester composition. Thus, the weight percent of ***thiol*** groups can be stated as an average weight percent across all hydroxy ***thiol*** ester molecules. DETD As an embodiment of the present invention, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of at least 1 ester groups and an average of at least 1 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule. As an embodiment of the present invention, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule. DETD Minimally, in some embodiments, the hydroxy ***thiol*** ester comprises at least one ester, at least one ***thiol*** group, and at least one hydroxy group. Because the hydroxy ***thiol*** ester is prepared from epoxidized unsaturated esters, the hydroxy ***thiol*** ester can contain the same number of ester groups as the epoxidized unsaturated esters. In an embodiment, the hydroxy ***thiol***

ester
molecules have an average of at least 1.5 ester groups per
hydroxy ***thiol*** ester molecule. Alternatively, the hydroxy
thiol
ester molecules have an average of at least 2 ester groups per
hydroxy ***thiol*** ester molecule; alternatively, an average of at
least 2.5
ester groups per hydroxy ***thiol*** ester molecule; or
alternatively, an average of at least 3 ester groups per hydroxy
thiol ester molecule. In other embodiments, the hydroxy
thiol esters have an average of from 1.5 to 8 ester
groups per
hydroxy ***thiol*** ester molecule; alternatively, an average
of
from 2 to 7 ester groups per hydroxy ***thiol*** ester
molecule;
alternatively, an average of from 2.5 to 5 ester groups per
hydroxy ***thiol*** ester molecule; or alternatively, an average of
from 3 to
4 ester groups per hydroxy ***thiol*** ester molecule. In yet
other
embodiments, the .alpha.-hydroxy ***thiol*** ester comprises
an
average of 3 ester groups per hydroxy ***thiol*** ester
molecule or
alternatively, an average of 4 ester groups per hydroxy
thiol
ester molecule.
DETD In some embodiments, the hydroxy group and the ***thiol***
group
are combined in the same group, which produces the .alpha.-
hydroxy
thiol group. In other embodiments, the ***thiol***
group and
the hydroxy or alcohol group are not in the same group. When this
occurs, to produce the hydroxy ***thiol*** ester composition,
the
alcohol group is added independently of the ***thiol***
group. For
example, as another embodiment of the present invention, the
hydroxy
thiol ester composition advantageously includes hydroxy
thiol ester molecules. The hydroxy ***thiol***
ester
molecules have an average of at least 1.5 ester groups, an
average of at
least 1.5 ***thiol*** groups, and an average of at least 1.5
alcohol
groups per hydroxy ***thiol*** ester molecule.
DETD Minimally, in some embodiments, the hydroxy ***thiol***
ester
comprises at least one ***thiol*** group per hydroxy
thiol
ester molecule. In an embodiment, the hydroxy ***thiol***
ester
molecules have an average of at least 1.5 ***thiol*** groups
per

hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2.5 ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of at least 3 ***thiol*** groups per hydroxy ***thiol*** ester molecule. In other embodiments, the hydroxy ***thiol*** ester molecules have an average of from 1.5 to 9 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 3 to 8 ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2 to 4 ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 4 to 8 ***thiol*** groups per hydroxy ***thiol*** ester.

DETD Minimally, in some embodiments, the hydroxy ***thiol*** ester composition comprises an average of at least 1 hydroxy or alcohol group per hydroxy ***thiol*** ester molecule. In some embodiments, the hydroxy ***thiol*** ester composition comprises an average of at least 1.5 hydroxy groups per hydroxy ***thiol*** ester molecule; alternatively, average of at least 2 hydroxy groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2.5 hydroxy groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of at least 3 hydroxy groups per ***thiol*** ester molecule. In other embodiments, the ***thiol*** ester composition comprises an average of from 1.5 to 9 hydroxy groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 3 to 8 hydroxy groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2 to 4 hydroxy groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 4 to 8 hydroxy groups per hydroxy ***thiol*** ester molecule.

DETD In yet other embodiments, the number of hydroxy groups can be stated as an average molar ratio of hydroxy group to ***thiol*** groups. Minimally, in some embodiments, the molar ratio of hydroxy groups to ***thiol*** groups is at least 0.25. In some embodiments, the molar ratio of hydroxy groups to ***thiol*** groups is at least 0.5;

alternatively, at least 0.75; alternatively, at least 1.0; alternatively, at least 1.25; or alternatively, at least 1.5. In other embodiments, the molar ratio of hydroxy groups to ***thiol*** groups ranges from 0.25 to 2.0; alternatively, from 0.5 to 1.5; or alternatively, from 0.75 to 1.25.

DETD In embodiments where the hydroxy ***thiol*** esters are produced from an epoxidized unsaturated ester, the hydroxy ***thiol*** esters can be described as containing ester groups and .alpha.-hydroxy ***thiol*** groups. The number of ester groups and the number of .alpha.-hydroxy ***thiol*** groups are independent elements and as such the hydroxy ***thiol*** esters can be described as having any combination of ester groups and .alpha.-hydroxy ***thiol*** groups described herein. Minimally, the hydroxy ***thiol*** ester comprises an average of at least 1 .alpha.-hydroxy ***thiol*** group per hydroxy ***thiol*** ester molecule. In some embodiments, the hydroxy ***thiol*** ester composition comprises an average of at least 1.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 2.5 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of at least 3 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule. In other embodiments, the hydroxy ***thiol*** ester composition comprises an average of from 1.5 to 9 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 3 to 8 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of from 2 to 4 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 4 to 8 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

DETD The hydroxy ***thiol*** esters can be produced by contacting an epoxidized ester derived from an unsaturated ester (i.e., epoxidized unsaturated ester), as described herein. In some instances it can be desirable to have ***epoxide*** groups present in the hydroxy

thiol ester composition. While in other embodiments, it can be desirable to minimize the number of epoxy groups present in the hydroxy

thiol ester composition. Thus, the presence of residual ***epoxide*** groups can be another separate functional group used to describe the hydroxy ***thiol*** ester.

DETD The presence of ***epoxide*** groups in the hydroxy ***thiol*** ester can be independently described as an average number of ***epoxide*** groups per hydroxy ***thiol*** ester, a molar ratio of ***epoxide*** groups to ***thiol*** groups, a molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups, or any combination thereof. In some embodiments, the hydroxy ***thiol*** ester molecules comprise an average of less than 2 ***epoxide*** groups per hydroxy ***thiol*** ester molecule, i.e., the hydroxy ***thiol*** ester molecules have a molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups of less than 2. Alternatively, the hydroxy ***thiol*** ester comprises an average of less than 1.5 ***epoxide*** groups per hydroxy ***thiol*** ester molecule; alternatively, an average of less than 1 ***epoxide*** group per hydroxy ***thiol*** ester molecule; alternatively, an average of less than 0.75 ***epoxide*** groups per hydroxy ***thiol*** ester molecule; or alternatively, an average of less than 0.5 ***epoxide*** groups per hydroxy ***thiol*** ester molecule.

In other embodiments, the molar ratio of ***epoxide*** groups to ***thiol*** groups averages less than 1.5. Alternatively, the molar ratio of ***epoxide*** groups to ***thiol*** groups averages less than 1; alternatively, averages less than 0.75; alternatively, averages less than 0.5; alternatively, averages less than 0.25; or alternatively, averages less than 0.1. In yet other embodiments, the molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups averages less than 1.5. Alternatively, the molar ratio of ***epoxide*** groups to .alpha.-hydroxy ***thiol*** groups averages less than 1; alternatively, averages less than 0.75; alternatively, averages less than 0.5; alternatively, averages less than 0.25; or alternatively, averages less than 0.1.

DETD In some embodiments, the hydroxy ***thiol*** ester composition is substantially free of ***epoxide*** groups.

DETD In other embodiments, the hydroxy ***thiol*** ester can be described by the average amount of ***thiol*** sulfur present in hydroxy ***thiol*** ester. In an embodiment, the hydroxy ***thiol*** ester molecules have an average of at least 2.5 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 5 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; alternatively, an average of at least 10 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; or alternatively, an average of greater than 15 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule. In an embodiment, the hydroxy ***thiol*** ester molecules have an average of from 5 to 25 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; alternatively, an average of from 5 to 20 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; alternatively, an average of from 6 to 15 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule; or alternatively, an average of from 8 to 10 weight percent ***thiol*** sulfur per hydroxy ***thiol*** ester molecule.

DETD In some embodiments, at least 20 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group. In some embodiments, at least 20 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group. In some embodiments, at least 60 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group; alternatively, at least 70 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group. Yet in other embodiments, at least 80 percent of the total side chains include the .alpha.-hydroxy ***thiol*** group.

DETD In some aspects, greater than 20 percent of the hydroxy ***thiol*** ester molecule total side chains contain sulfur. In some aspects, greater than 40 percent of the hydroxy ***thiol*** ester molecule total side chains contain sulfur. In some aspects, greater than 60 percent of the hydroxy ***thiol*** ester molecule total side chains

contain sulfur; alternatively, greater than 70 percent of the total side chains contain sulfur; or alternatively, greater than 80 percent of the total side chains contain sulfur.

DETD In particular embodiments, the epoxidized unsaturated ester used in the synthesis of the hydroxy ***thiol*** ester is produced from the epoxidized unsaturated ester composition that includes an epoxidized natural source oil. Because the natural source oils have particular compositions regarding the number of ester groups present, the hydroxy ***thiol*** ester will have about the same number of ester groups as the feedstock natural source oil. Other independent properties that are described herein can be used to further describe the hydroxy ***thiol*** ester.

DETD In other embodiments, the epoxidized unsaturated ester used to produce the hydroxy ***thiol*** ester is produced from synthetic (or semi-synthetic) unsaturated ester oils. Because the synthetic ester oils can have particular compositions regarding the number of ester groups present, the hydroxy ***thiol*** ester would have about the same number of ester groups as the synthetic ester oil. Other, independent properties of the unsaturated ester, whether the unsaturated ester includes natural source or synthetic oils, can be used to further describe the hydroxy ***thiol*** ester composition.

DETD The hydroxy ***thiol*** ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an epoxidized unsaturated ester composition and can be further limited by the process as described herein. The hydroxy ***thiol*** containing natural source oil can also be described using an average molecular weight or an average molecular weight of the side chains.

DETD Cross-Linked ***Thiol*** Ester Compositions

DETD In an aspect, the present invention relates to a cross-linked ***thiol*** ester composition. Generally, the cross-linked ***thiol*** ester molecules are oligomers of ***thiol*** esters that are connected together by polysulfide linkages --S.sub.x-- wherein x is an integer greater 1. As the cross-linked ***thiol*** ester is described as an oligomer of ***thiol*** esters, the ***thiol*** esters can be described as the monomer from which the cross-

linked
 thiol esters are produced.

DETD In an aspect, the cross-linked ***thiol*** ester composition comprises a ***thiol*** ester oligomer having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is an integer greater than 1. In an aspect, the polysulfide linkage may be the polysulfide linkage --S.sub.Q--, wherein Q is 2, 3, 4, or mixtures thereof. In other embodiments, Q can be 2; alternatively, 3; or alternatively, 4.

DETD In an aspect, the cross-linked ***thiol*** ester composition comprises a ***thiol*** ester oligomer having at least 3 ***thiol*** ester monomers connected by polysulfide linkages; alternatively, 5 ***thiol*** ester monomers connected by polysulfide linkages; alternatively, 7 ***thiol*** ester monomers connected by polysulfide linkages; or alternatively, 10 ***thiol*** ester monomers connected by polysulfide linkages. In yet other embodiments, the cross-linked ***thiol*** ester composition comprises a ***thiol*** ester oligomer having from 3 to 20 ***thiol*** ester monomers connected by polysulfide linkages; alternatively, from 5 to 15 ***thiol*** ester monomers connected by polysulfide linkages; or alternatively, from 7 to 12 ***thiol*** ester monomers connected by polysulfide linkages.

DETD In an aspect, the cross-linked ***thiol*** ester composition comprises ***thiol*** ester monomers and ***thiol*** ester oligomers. In some embodiments, the cross-linked ***thiol*** ester composition has a combined ***thiol*** ester monomer and ***thiol*** ester oligomer average molecular weight greater than 2,000. In other embodiments, the cross-linked ***thiol*** ester composition has a combined ***thiol*** ester monomer and ***thiol*** ester oligomer average molecular weight greater than 5,000; or alternatively, greater than 10,000. In yet other embodiments, the cross-linked ***thiol*** ester composition has a combined ***thiol*** ester monomer and ***thiol*** ester oligomer average molecular weight ranging from 2,000 to 20,000; alternatively, from 3,000 to 15,000; or alternatively, from 7,500 to 12,500.

DETD In an aspect, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total ***thiol*** sulfur content greater than 0.5. In other embodiments, the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total ***thiol*** sulfur content greater than 1; alternatively, greater than 2;

alternatively,
greater than 4. In yet other embodiments, the ***thiol***
ester monomers and the ***thiol*** ester oligomers have a total
thiol sulfur content from 0.5 to 8; alternatively, from
4 to 8;
or alternatively, 0.5 to 4.

DETD In an aspect, the ***thiol*** ester monomers and
thiol
ester oligomers have a total sulfur content greater than 8. In
some
embodiments, the ***thiol*** ester monomers and ***thiol***
ester oligomers have a total sulfur content greater than 10;
alternatively, greater than 12. In yet other embodiments, the
thiol ester monomers and ***thiol*** ester
oligomers have a
total sulfur content ranging from 8 to 15 weight percent;
alternatively,
from 9 to 14; or alternatively, from 10 to 13.

DETD The cross-linked ***thiol*** ester compositions can also be
described as a product produced by the process comprising
contacting a
thiol ester with oxidizing agent and can be further
limited by
the process as described herein.

DETD The present invention advantageously includes sulfide-containing
ester
compositions as embodiments of the present invention. Generally,
the
sulfide-containing ester compositions can be described as
containing
molecules having at least one ester group and a least one sulfide
group
within each molecule. The sulfide-containing esters used in the
present
invention can be produced by contacting either an unsaturated
ester or
an epoxidized unsaturated ester with a ***thiol*** containing
compound as described herein.

DETD The feedstock unsaturated esters can contain multiple carbon-
carbon
double bonds per unsaturated ester molecule. The carbon-carbon
double
bond reactivity and statistical probability, however, dictate
that each
sulfide-containing ester molecule of the ***thiol*** -
containing
ester composition produced from the unsaturated ester composition
will
not have the same number of sulfide groups, number of unreacted
carbon-carbon double bonds, molar ratio of carbon-carbon double
bonds to
sulfide groups, molar ratio of cyclic sulfides to ***thiol***
groups
and other herein disclosed quantities of functional groups and
molar
ratios. Additionally, the feedstock unsaturated esters can also
comprise
a mixture of individual unsaturated esters having a different
number of

carbon-carbon double bonds and/or ester groups. Many of these properties are discussed herein as an average number of the groups per sulfide-containing ester molecule within the sulfide-containing composition or average ratio per ***thiol*** -containing ester molecule within the sulfide-containing ester composition.

DETD In embodiments related to the sulfide-containing ester that is produced from an epoxidized unsaturated ester, the feedstock epoxidized unsaturated esters can contain multiple ***epoxide*** groups per unsaturated ester molecule. Individual ***epoxide*** group reactivity and statistical probability dictate that each sulfide-containing ester molecule of the sulfide-containing ester composition produced from the unsaturated ester composition will not have the same number of sulfide groups, number of unreacted ***epoxide*** groups, molar ratio of ***epoxide*** groups to sulfide groups, and other herein disclosed quantities of functional groups and molar ratios. Additionally, the feedstock epoxidized unsaturated esters can also comprise a mixture of individual epoxidized unsaturated ester molecules having a different number of ***epoxide*** groups and/or ester groups. Thus, many of these properties are described as an average number of the groups per sulfide-containing ester molecules within the sulfide-containing ester composition or average ratio per ***thiol*** -containing ester molecule within the sulfide-containing ester composition.

DETD Minimally, in some embodiments, the sulfide-containing esters comprise at least one ester group per sulfide-containing ester molecule. In some embodiments, the sulfide-containing ester has an average of at least 1.5 ester groups per sulfide-containing ester molecule. Alternatively, the sulfide-containing ester molecules have an average of at least 2 ester groups per sulfide-containing ester molecule; alternatively, an average of at least 2.5 ester groups per sulfide-containing ester molecule; or alternatively, an average of at least 3 ester groups per sulfide-containing ester molecule. In other embodiments, the sulfide-containing esters have an average of from 1.5 to 9 ester groups per sulfide-containing ester molecule; alternatively, an average of from 1.5 to 8 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2 to 8 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2 to 7 ester groups per sulfide-containing ester molecule; alternatively,

an average of from 2.5 to 5 ester groups per sulfide-containing ester molecule; alternatively, an average of from 3 to 5 ester groups per sulfide-containing ester molecule; or alternatively, an average of from 3 to 4 ester groups per sulfide-containing ester molecule. In yet other embodiments, the hydroxy ***thiol*** -containing ester comprises an average of about 3 ester groups per sulfide-containing ester molecule; or alternatively, an average of about 4 ester groups per sulfide-containing ester molecule.

DETD In some embodiments, R.sup.3 comprises at least one functional group.

In one aspect, the functional group is selected from the group consisting of a hydroxy group, a carboxylic acid group, a carboxylic ester group, an amine group, a sulfide group, and a second ***thiol*** group. In some aspects, R.sup.3 comprises at least two functional groups. In some aspects, the functional groups are selected from the group consisting of a hydroxy group, carboxylic acid group, a carboxylic ester group, an amine group, a sulfide group, a second ***thiol*** group, and mixtures thereof.

DETD The sulfide-containing ester compositions can also be described as a

product produced by the process comprising contacting an unsaturated ester with a ***mercaptan*** and can be further limited by the process as described herein. In other embodiments, the sulfide-containing ester composition can also be described as a product produced by a process comprising contacting an epoxidized unsaturated ester with a ***mercaptan*** and can be further limited by the process as described herein.

DETD Generally, the thioacrylate ester composition can be described as comprising thioacrylate molecules having at least one ester group in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule and at least one thioacrylate group. The ester group(s) that are in addition to any acrylate or thioacrylate groups present in the thioacrylate molecule are hereinafter referred to as "supplementary ester group(s)." The thioacrylate ester composition described herein can be produced by contacting an acrylate composition with a ***thiol*** -containing ester composition and/or a

hydroxy ***thiol*** -containing ester composition, both of which are described herein.

DETD The feedstock ***thiol*** ester compositions and/or hydroxy
 thiol ester compositions can comprise a mixture of molecules that have an average quantity of ester groups, ***thiol*** groups, hydroxy groups, and other groups and molar ratios described herein.

 Additionally, individual ***thiol*** and hydroxy group reactivity within the ***thiol*** -containing ester compositions and/or hydroxy ***thiol*** ester compositions and statistical probability dictate that each thioacrylate ester molecule of the thioacrylate ester composition produced may not have the same number of ester groups, thioacrylate groups, acrylate groups, and other herein disclosed quantities of functional groups, moieties, and molar ratios.

Thus, many of the properties of the thioacrylate ester molecules within the thioacrylate ester composition are described as using an average number of the groups per thioacrylate ester molecule within the thioacrylate ester composition or as an average ratio per thioacrylate ester molecule within the thioacrylate ester composition.

DETD The thioacrylate ester can also be described as a product produced by the process that includes contacting a ***thiol*** -containing ester composition with an acrylate composition and can be further limited by the process described herein. In other embodiments, the thioacrylate ester composition can also be described as a product produced by a process that includes contacting a hydroxy ***thiol*** -containing ester composition with an acrylate composition and can be further limited by the process described herein.

DETD The present invention advantageously provides a sulfonic acid-containing ester as an embodiment of the present invention. Generally, the sulfonic acid-containing ester of the present invention includes sulfonic acid-containing ester molecules having at least one ester group and a least one sulfonic acid group. The sulfonic acid-containing ester described herein can be produced by contacting a ***thiol*** ester with an oxidizing agent as described herein. Because the feedstock for the production of the sulfonic acid-containing ester can include multiple ***thiols*** groups, ***thiol*** group

reactivity and statistical probability dictate that each sulfonic acid-containing ester molecule of the sulfonic acid-containing ester

will not have the same number of sulfonic acid groups.

Additionally, the

feedstock ***thiol*** ester can also include a mixture of individual

thiol ester molecules having different numbers of ***thiol***

groups and/or ester groups. Thus, many of the groups present in the

sulfonic acid-containing ester are described herein as an average number

of the groups per sulfonic acid-containing ester molecule or an average

ratio per sulfonic acid-containing ester molecule within the sulfonic

acid-containing ester.

DETD In some embodiments of the present invention, the sulfonic acid ester

is substantially free of ***thiol*** groups.

DETD The sulfonic acid-containing ester can also be described as a product

produced by the process comprising contacting a ***thiol*** ester

with an oxidizing agent described herein.

DETD Process for Making a ***Thiol*** Ester Composition

DETD The present invention advantageously provides processes for producing a

thiol ester composition as embodiments of the present invention.

As an embodiment, the present invention advantageously includes a process to produce a ***thiol*** ester composition by

contacting

hydrogen sulfide and an unsaturated ester composition containing unsaturated esters and reacting the hydrogen sulfide and

unsaturated

esters to form or produce the ***thiol*** ester composition.

As

another embodiment of the present invention, a process to produce the

thiol ester composition is advantageously provided. In this

embodiment, the process includes contacting a composition comprising a

polyol with a composition comprising a ***thiol*** containing carboxylic acid composition and reacting the polyol and

thiol

containing carboxylic acid composition to form the ***thiol***

ester

composition.

DETD In some embodiments of the present invention that include producing

thiol ester compositions, the unsaturated ester composition is a

natural source oil. In an aspect, the unsaturated ester composition is

soybean oil or alternatively castor oil. Other suitable types of unsaturated ester compositions are described herein and can be

used in

the processes for producing the ***thiol*** ester compositions.

DETD ***Thiol*** Esters from Unsaturated Esters

DETD As an embodiment of the present invention, the ***thiol*** esters described herein can be produced by a process comprising contacting hydrogen sulfide and an unsaturated ester composition and reacting hydrogen sulfide and the unsaturated ester composition to form the ***thiol*** ester composition. In one embodiment, the unsaturated ester composition includes unsaturated esters having an average of at least 1.5 ester groups and an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. In this embodiment, the ***thiol*** ester composition includes ***thiol*** ester molecules having a molar ratio of cyclic sulfides to ***thiol*** groups of less than 1.5.

DETD The processes for producing the ***thiol*** ester composition can be applied to any of the unsaturated esters described herein and used to produce any of the ***thiol*** esters described herein. The process for producing the ***thiol*** ester composition can also include any additional process steps or process conditions described herein.

DETD The hydrogen sulfide to molar equivalents of unsaturated ester carbon-carbon double bonds molar ratio utilized in the process to produce the ***thiol*** ester composition can be any molar ratio that produces the desired ***thiol*** ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the equation:
$$\frac{UES\ GMW}{UES\ Mass} \times UES\ C.dbd.C$$
 In this equation, UES GMW is the average gram molecular weight of the unsaturated ester, UES Mass is the mass of the feedstock unsaturated ester, and UES C.dbd.C is the average number of double bonds per unsaturated ester molecule. In some embodiments, the ***thiol*** ester molecules have a molar ratio of the hydrogen sulfide to the unsaturated ester carbon-carbon double bonds of greater than 2. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio can be

from 2 to 500; alternatively, from 5 to 200; alternatively, from 10 to 100; or alternatively, from 100 to 200.

DETD When a continuous reactor is used, a feed unsaturated ester weight hourly space velocity ranging from 0.1 to 5 can be used to produce the desired ***thiol*** ester. Alternatively, the feed unsaturated ester weight hourly space velocity ranges between 0.1 to 5; alternatively, from 0.1 to 2. Alternatively, the feed unsaturated ester weight hourly space velocity is 0.1; alternatively, the feed unsaturated ester weight hourly space velocity is 0.25; or alternatively, the feed unsaturated ester weight hourly space velocity is 2.

DETD The time required for the reaction of the unsaturated ester and hydrogen sulfide can be any time required to form the described ***thiol*** ester. Generally, the time required for the reaction of the unsaturated ester and hydrogen sulfide is at least 5 minutes.

In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15 minutes to 36 hours.

DETD In embodiments, the process to produce the ***thiol*** ester further comprises a step to remove excess or residual hydrogen sulfide after reacting the hydrogen sulfide and the unsaturated ester composition. In some embodiments, the ***thiol*** ester is vacuum stripped. In some embodiments, the ***thiol*** ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the ***thiol*** ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged ***thiol*** ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged ***thiol*** ester comprises less than 0.05 weight percent sulfur; alternatively, less than 0.025 weight percent hydrogen sulfide; or

alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The reaction between the unsaturated ester and hydrogen sulfide can be performed at any temperature capable of forming the ***thiol*** ester. In some embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature greater than -20.degree. C. In other embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature from -20.degree. C. to 200.degree. C.; alternatively, from 120.degree. C. to 240.degree. C.; alternatively, from 170.degree. C. to 210.degree. C.; alternatively, from 185.degree. C. to 195.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD ***Thiol*** esters having a low cyclic sulfide content can be produced using the disclosed process. In an aspect, the process for producing the ***thiol*** ester forms or produces a ***thiol*** ester having a molar ratio of cyclic sulfide to ***thiol*** groups of less than 1.5. Additional cyclic sulfide to ***thiol*** groups molar ratios are disclosed herein.

DETD In addition to lower cyclic sulfide content, ***thiol*** esters having a low carbon-carbon double bond to ***thiol*** group molar ratio can also be produced using the disclosed process. In an aspect, the process described herein produces the ***thiol*** ester having a carbon-carbon double bond to ***thiol*** group molar ratio of less than 1.5. Additional carbon-carbon double bond to ***thiol*** group molar ratios are disclosed herein.

DETD In some aspects, the process described herein produces the ***thiol*** ester molecules having an average of greater than 5 weight percent ***thiol*** sulfur. Additional ***thiol*** sulfur contents are disclosed herein. In other aspects, the process for producing a ***thiol*** ester forms a ***thiol*** ester having greater than 40 percent of the ***thiol*** ester total side

chains include sulfur. Other percentages of the ***thiol*** ester total side chains that include sulfur are disclosed herein.

DETD In some embodiments, the process for producing a ***thiol*** ester composition includes contacting an unsaturated ester and hydrogen sulfide and reacting the unsaturated ester and the hydrogen sulfide to form a ***thiol*** ester. The ***thiol*** ester comprises ***thiol*** ester molecules that have a ratio of cyclic sulfide to ***thiol*** groups of less than 1.5.

DETD ***Thiol*** Ester from a Polyol and a ***Thiol*** Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process to produce the ***thiol*** ester composition is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative and reacting the polyol and ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative to produce the ***thiol*** ester composition. This process can be applied to any polyol, ***thiol*** containing carboxylic acid, or ***thiol*** containing carboxylic acid derivative described herein. The process for producing the ***thiol*** ester composition can also include any additional process steps or process conditions described herein. Additionally, the process for producing the ***thiol*** ester composition can form any ***thiol*** ester described herein.

DETD In some embodiments, the ***thiol*** ester composition includes ***thiol*** ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 ***thiol*** groups per ***thiol*** ester molecule.

DETD The polyol used to produce the ***thiol*** ester by contacting a polyol and a ***thiol*** carboxylic acid and/or ***thiol*** carboxylic acid equivalent (for example a ***thiol*** carboxylic acid methyl ester) can be any polyol or mixture of polyols that can produce the described ***thiol*** containing ester.

DETD In one aspect, the polyol used to produce the ***thiol*** ester can comprise from 2 to 20 carbon atoms. In other embodiments, the polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7 carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments,

the polyol may be a mixture of polyols having an average of 2 to
20 carbon atoms; alternatively, an average of from 2 to 10 carbon
atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively
an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the ***thiol***
ester can have any number of hydroxy groups needed to produce the
thiol ester as described herein. In some embodiments,
the polyol
has 2 hydroxy groups; alternatively 3 hydroxy groups;
alternatively, 4
hydroxy groups; alternatively, 5 hydroxy groups; or
alternatively, 6
hydroxy groups. In other embodiments, the polyol comprises at
least 2
hydroxy groups; alternatively at least 3 hydroxy groups;
alternatively,
at least 4 hydroxy groups; or alternatively, at least 5 hydroxy
groups;
at least 6 hydroxy groups. In yet other embodiments, the polyol
comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4
hydroxy
groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the ***thiol***
ester is a mixture of polyols. In an embodiment, the mixture of
polyols
has an average of at least 1.5 hydroxy groups per polyol
molecule. In
other embodiments, the mixture of polyols has an average of at
least 2
hydroxy groups per polyol molecule; alternatively, an average of
at
least 2.5 hydroxy groups per polyol molecule; alternatively, an
average
of at least 3.0 hydroxy groups per polyol molecule; or
alternatively, an
average of at least 4 hydroxy groups per polyol molecule. In yet
another
embodiments, the mixture of polyols has an average of 1.5 to 8
hydroxy
groups per polyol molecule; alternatively, an average of 2 to 6
hydroxy
groups per polyol molecule; alternatively, an average of 2.5 to 5
hydroxy groups per polyol molecule; alternatively, an average of
3 to 4
hydroxy groups per polyol molecule; alternatively, an average of
2.5 to
3.5 hydroxy groups per polyol molecule; or alternatively, an
average of
2.5 to 4.5 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to
produce
the ***thiol*** ester has a molecular weight or average
molecular
weight less than 500. In other embodiments, the polyol or mixture
of
polyols have a molecular weight or average molecular weight less

than 300; alternatively less than 200; alternatively, less than 150;
 or alternatively, less than 100.
 DETD The ***thiol*** carboxylic acid and/or ***thiol***
 carboxylic acid equivalent used to produce the ***thiol*** ester by
 contacting a polyol and a ***thiol*** carboxylic acid and/or
 thiol carboxylic acid equivalent can be any ***thiol*** carboxylic
 acid mixture comprising ***thiol*** carboxylic acids,
 thiol carboxylic acid equivalent or mixture comprising ***thiol***
 carboxylic acid equivalents that can produce the described
 thiol containing ester. When talking about the characteristics
 thiol carboxylic acid equivalent or ***thiol*** carboxylic acid
 equivalents, properties such as number of carbon atoms, average
 number of carbon atom, molecular weight or average molecular weight,
 number of ***thiol*** group, and average number of ***thiol***
 groups, one will understand the these properties will apply to the portion of
 the ***thiol*** carboxylic acid equivalent which adds to the
 polyol to form the ***thiol*** ester.
 DETD In an aspect, the ***thiol*** carboxylic acid and/or
 thiol carboxylic acid equivalent used to produce the ***thiol***
 ester comprises from 2 to 28 carbon atoms. In an embodiment, the
 thiol carboxylic acid and/or ***thiol*** carboxylic acid equivalent
 comprises from 4 to 26 carbon atoms; alternatively, from 8 to 24
 carbon atoms; alternatively, from 12 to 24 carbon atoms; or
 alternatively, from 14 to 20 carbon atoms. In other embodiments, a mixture comprising
 thiol carboxylic acid and/or mixture comprising
 thiol carboxylic acid equivalents has an average of 2 to 28 carbon
 atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively,
 from 4 to 26 carbon atoms per carboxylic acid and/or carboxylic acid
 equivalent; alternatively, from 8 to 24 carbon atoms per
 carboxylic acid and/or carboxylic acid equivalent; alternatively, from 12 to 24
 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; or
 alternatively, from 14 to 20 carbon atoms per carboxylic acid
 and/or carboxylic acid equivalent.
 DETD In another aspect, the ***thiol*** carboxylic acid and/or
 thiol carboxylic acid equivalent used to produce the

thiol ester has at least 1 ***thiol*** group;
 alternatively
 2 ***thiol*** groups. In some embodiments, a mixture
 comprising
 thiol carboxylic acid and/or mixture comprising
 thiol
 carboxylic acid equivalents has an average of from 0.5 to 3
 thiol groups per carboxylic acid and/or carboxylic acid
 equivalent; alternatively, an average of from 1 to 2
 thiol
 groups per carboxylic acid and/or carboxylic acid equivalent.
 DETD In another aspect, the ***thiol*** carboxylic acid and/or
 thiol carboxylic acid equivalent used to produce the
 thiol ester has a molecular weight greater than 100;
 alternatively greater than 180; alternatively greater than 240;
 or
 alternatively greater than 260. In other embodiments, the
 thiol
 carboxylic acid and/or ***thiol*** carboxylic acid equivalent
 has a
 molecular weight from 100 to 500; alternatively, from 120 to 420;
 alternatively, from 180 to 420; alternatively, from 240 to 420; a
 mixture or alternatively, from 260 to 360. In some embodiments, a
 mixture comprising ***thiol*** carboxylic acid and/or mixture
 comprising ***thiol*** carboxylic acid equivalents has an
 average
 molecular weight greater than 100 per carboxylic acid and/or
 carboxylic
 acid equivalent; alternatively greater than 180 per carboxylic
 acid
 and/or carboxylic acid equivalent; alternatively greater than 240
 per
 carboxylic acid and/or carboxylic acid equivalent; or
 alternatively
 greater than 260 per carboxylic acid and/or carboxylic acid
 equivalent.
 In yet other embodiments, the mixture comprising of ***thiol***
 carboxylic acid and/or mixture comprising ***thiol***
 carboxylic
 acid equivalents has an average molecular weight from 100 to 500
 per
 carboxylic acid and/or carboxylic acid equivalent; alternatively,
 from
 120 to 420 per carboxylic acid and/or carboxylic acid equivalent;
 alternatively, from 180 to 420 per carboxylic acid and/or
 carboxylic
 acid equivalent; alternatively, from 240 to 420 per carboxylic
 acid
 and/or carboxylic acid equivalent; a mixture or alternatively,
 from 260
 to 360 per carboxylic acid and/or carboxylic acid equivalent.
 DETD In some aspects, the reaction between the polyol and the
 thiol
 containing carboxylic acid and/or ***thiol*** containing
 carboxylic
 acid derivative occurs in the presence of a solvent. In other
 aspects
 the reaction between the polyol and the ***thiol***
 containing
 carboxylic acid and/or ***thiol*** containing carboxylic acid

derivative occurs in the substantial absence of a solvent. In aspects wherein the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative occurs in the presence of a solvent, the solvent is selected from the group consisting of an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof. Generally, the solvent, regardless of its chemical class, can include from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, and any mixture thereof. DETD When a solvent is used for the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester oil; alternatively, less than 15 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative; alternatively, less than 10 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative; or alternatively, less than 5 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative; alternatively, from 3 times to 15 times the mass of the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative, or alternatively, from 5

times to
10 times the mass of the ***thiol*** containing carboxylic acid
acid
and/or ***thiol*** containing carboxylic acid derivative.
DETD The equivalent of ***thiol*** containing carboxylic acid
and/or
thiol containing carboxylic acid derivative carboxylic acid
groups to equivalents of polyol hydroxy groups molar ratio
(hereinafter
"carboxylic acid group to polyol hydroxy group molar ratio")
utilized in
the process to produce the ***thiol*** ester composition can
be any
carboxylic acid group to polyol hydroxy group molar ratio that
produces
the desired ***thiol*** ester composition. In some
embodiments, the
carboxylic acid group to polyol hydroxy group molar ratio is
greater
than 0.4. In other embodiments, the carboxylic acid group to
polyol
hydroxy group molar ratio is greater than 0.6; alternatively,
greater
than 0.8; alternatively, greater than 1; or alternatively,
greater than
1.1. In other embodiments, the carboxylic acid group to polyol
hydroxy
group molar ratio can range from 0.4 to 1.3; alternatively, from
0.6 to
1.2, or alternatively, from 0.8 to 1.1.
DETD In some aspects, the reaction between the polyol and the
thiol
containing carboxylic acid and/or ***thiol*** containing
carboxylic
acid derivative is catalyzed. In some embodiments, the catalyst
is a
mineral acid, such as sulfuric or phosphoric acid. In other
embodiments,
the catalyst is an organic acid. In embodiments, for example, the
organic acid is methane sulfonic acid or toluene sulfonic acid.
Other
suitable types of catalyst will be apparent to those of skill in
the art
and are to be considered within the scope of the present
invention.
DETD The reaction of the polyol and the ***thiol*** containing
carboxylic acid and/or ***thiol*** containing carboxylic acid
derivative can occur in a batch reactor or a continuous reactor,
as
described herein. The reaction between the polyol and the
thiol
containing carboxylic acid and/or ***thiol*** containing
carboxylic
acid derivative can be performed at any temperature capable of
forming
the ***thiol*** ester. In some embodiments, the polyol and
the
thiol containing carboxylic acid and/or ***thiol***
containing carboxylic acid derivative can be reacted at a

temperature
greater than 20.degree. C. In other embodiments, the polyol and
the
thiol containing carboxylic acid and/or ***thiol***
containing carboxylic acid derivative can be reacted at a
temperature
greater than 50.degree. C.; alternatively, greater than
75.degree. C.;
or alternatively, greater than 100.degree. C. In yet other
embodiments,
the polyol and the ***thiol*** containing carboxylic acid
and/or
thiol containing carboxylic acid derivative can be
reacted at a
temperature from 20.degree. C. to 250.degree. C.; alternatively,
from
50.degree. C. to 200.degree. C.; alternatively, from 75.degree.
C. to
175.degree. C.; or alternatively, from 100.degree. C. to
150.degree. C.
DETD The time required for the reaction of the polyol and the
thiol
containing carboxylic acid and/or ***thiol*** containing
carboxylic
acid derivative can be any time required to form the described
thiol ester oil. Generally, the reaction time of the
polyol and
the ***thiol*** containing carboxylic acid and/or
thiol
containing carboxylic acid derivative is at least 5 minutes. In
some
embodiments, the reaction time is at least 30 minutes;
alternatively, at
least 1 hour; or alternatively, at least 2 hours. In yet other
embodiments, the reaction time ranges from 5 minutes to 72 hours;
alternatively, from 30 minutes to 48 hours; alternatively, from 1
hour
minutes to 36 hours; or alternatively, from 2 hours and 24 hours.
DETD When a continuous reactor is used, a feed polyol weight
unsaturated
ester weight hourly space velocity ranging from 0.1 to 5 can be
used to
produce the desired ***thiol*** ester. Alternatively, the
feed
polyol weight hourly space velocity ranges between 0.1 to 5;
alternatively, from 0.1 to 2. Alternatively, the feed polyol
ester
weight hourly space velocity is 0.1; alternatively, the feed
polyol
weight hourly space velocity is 0.25; or alternatively, the feed
polyol
weight hourly space velocity is 2.
DETD The reaction between the polyol and the ***thiol***
containing
carboxylic acid and/or ***thiol*** containing carboxylic acid
derivative can be performed at any reaction pressure that
maintains the
polyol and the ***thiol*** containing carboxylic acid and/or
thiol containing carboxylic acid derivative in a liquid
state.

In some embodiments, the reaction between the polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative is performed at a pressure ranging from 0 psia to 2000 psia. In other embodiments, the reaction pressure ranges from 0 psia to 1000 psia; alternatively, from 0 psia and 500 psia; or alternatively, 0 psia to 300 psia.

DET D In some embodiments, the process to produce the ***thiol*** ester by reacting a polyol and the ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative can further include a step to remove excess or residual polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative once the polyol has reacted with the ***thiol*** containing carboxylic acid or ***thiol*** containing carboxylic acid derivative. In some embodiments, the ***thiol*** ester is vacuum stripped. In some embodiments, the ***thiol*** ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the ***thiol*** ester is sparged with an inert gas to remove excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative. In some embodiments, the ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged ***thiol*** ester comprises less than 5 excess polyol, ***thiol*** containing carboxylic acid, or ***thiol*** containing carboxylic acid derivative. In other embodiments, the stripped or sparged ***thiol*** ester comprises less than 2 weight percent excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative; alternatively, less than 1 weight percent excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative; or alternatively, less than 0.5 weight percent excess polyol, ***thiol*** containing carboxylic acid, and/or ***thiol*** containing carboxylic acid derivative.

DETD Process for Making Hydroxy ***Thiol*** Ester Composition

DETD The present invention advantageously provides processes for producing a

hydroxy ***thiol*** ester as embodiments of the present invention.

As an embodiment, the present invention includes a process to produce

the hydroxy ***thiol*** ester. The process comprises the steps of

contacting hydrogen sulfide and an epoxidized unsaturated ester composition and reacting the hydrogen sulfide and the epoxidized unsaturated ester to form the hydroxy ***thiol*** ester. As

another

embodiment of the present invention, another process to produce

the

hydroxy ***thiol*** ester is provided. In this embodiment,

the

process comprises the steps of contacting a composition

comprising a

polyol with a composition comprising an hydroxy ***thiol***

containing carboxylic acid or an hydroxy ***thiol***

containing

carboxylic acid derivative and reacting the polyol and the

hydroxy

thiol containing carboxylic acid or the hydroxy

thiol

containing carboxylic acid derivative to form the hydroxy

thiol

ester.

DETD Hydroxy ***Thiol*** Ester from Hydrogen Sulfide and an Epoxidized

Unsaturated Ester Composition

DETD As an embodiment of the present invention, the hydroxy

thiol

ester composition is produced by a process comprising the steps

of

contacting hydrogen sulfide and an epoxidized unsaturated ester composition and reacting the hydrogen sulfide and the epoxidized unsaturated ester to produce the hydroxy ***thiol*** ester composition.

DETD In some embodiments, the epoxidized unsaturated ester composition

includes epoxidized unsaturated esters that have an average of at least

1 ester groups and an average of at least 1 ***epoxide***

groups per

epoxidized unsaturated ester molecule.

DETD The process for producing or preparing the hydroxy ***thiol*** ester composition can be applied to any of the epoxidized

unsaturated

esters described herein and used to produce any hydroxy

thiol

ester described herein. The process for producing the hydroxy

thiol ester can also include any additional process

steps or

process conditions as described herein. Additionally, the process

for

producing the hydroxy ***thiol*** ester can form any hydroxy

thiol ester described herein.

DETD In some aspects, the hydroxy ***thiol*** ester is produced

by contacting hydrogen sulfide with the epoxidized natural source oil under the reaction conditions to form the hydroxy ***thiol*** ester in the presence of an optional catalyst. In some embodiments, the catalyst can be a heterogeneous catalyst or a homogeneous catalyst. Examples of suitable catalysts are described herein. Additional types of suitable catalysts will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The hydrogen sulfide to molar equivalents of ***epoxide*** groups in the epoxidized unsaturated ester (hereinafter "hydrogen sulfide to ***epoxide*** group molar ratio") utilized in the process to produce the hydroxy ***thiol*** ester can be any hydrogen sulfide to ***epoxide*** group molar ratio that produces the desired hydroxy ***thiol*** ester. The molar equivalents of epoxidized unsaturated ester epoxidized groups can be calculated by the equation:

##EQU2##

In this equation, EUES GMW is the average gram molecular weight of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES ***Epoxide*** is the average number of ***epoxide*** groups per epoxidized unsaturated ester molecule. In some embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio is greater than 0.2. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio ranges from 0.2 to 5; alternatively, from 0.5 to 4; or alternatively, from 0.75 to 3. In some embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio is greater than 2. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio can be from 0.2 to 500; alternatively, from 0.5 to 400; alternatively, from 1 to 300; alternatively, from 2 to 250; alternatively, 5 to 200; or alternatively,

from 10 to 100.

DETD The time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide can be any time required to form the described hydroxy ***thiol*** ester. Generally, the time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide is at least 15 minutes. In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of greater than 2.5 weight percent ***thiol*** sulfur. In some embodiments, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of greater than 5 weight percent ***thiol*** sulfur. Alternatively, in some embodiments, the hydroxy ***thiol*** ester molecules have an average ranging from 8 to 10 weight percent ***thiol*** sulfur.

DETD In other aspects, the process producing the hydroxy ***thiol*** ester composition includes producing hydroxy ***thiol*** ester molecules having an average of greater than 40 percent of the sulfide-containing ester total side chains comprise a sulfide group. Additional embodiments wherein the hydroxy ***thiol*** ester comprises a percentage of sulfide-containing ester total side chains are described herein.

DETD In embodiments, the process to produce the hydroxy ***thiol*** ester further comprises a step to remove residual hydrogen sulfide after reacting the hydrogen sulfide and the epoxidized unsaturated ester composition. In some embodiments, the hydroxy ***thiol*** ester is vacuum stripped. In some embodiments, the hydroxy ***thiol*** ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the hydroxy ***thiol*** ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the

inert gas
is nitrogen. Generally, the stripped or sparged hydroxy
thiol
ester comprises less than 0.1 weight percent hydrogen sulfide. In
other
embodiments, the stripped or sparged hydroxy ***thiol***
ester
comprises less than 0.05 weight percent hydrogen sulfide;
alternatively,
less than 0.025 weight percent hydrogen sulfide; or
alternatively, less
than 0.01 weight percent hydrogen sulfide.
DETD The reaction between the hydrogen sulfide and the epoxidized
unsaturated ester can be performed at any temperature capable of
forming
the hydroxy ***thiol*** ester. In some embodiments, the
epoxidized
unsaturated ester and hydrogen sulfide can be reacted at a
reaction
temperature greater than -20.degree. C. In other embodiments, the
reaction temperature is greater than 0.degree. C.; alternatively,
greater than 20.degree. C.; alternatively, greater than
50.degree. C.;
or alternatively, greater than 80.degree. C. In yet other
embodiments,
the reaction temperature ranges from -20.degree. C. to
200.degree. C.;
alternatively, from 20.degree. C. to 170.degree. C.; or
alternatively,
from 80.degree. C. to 140.degree. C.
DETD In another aspect, the process to produce a hydroxy
thiol
ester produces a hydroxy ***thiol*** ester having an
epoxide
group to ***thiol*** group molar ratio less than 3.3. In
another
aspect, the process to produce a hydroxy ***thiol*** ester
produces
a hydroxy ***thiol*** ester having an ***epoxide*** group
to
thiol group molar ratio less than 2. Other hydroxy
thiol
ester ***epoxide*** group to ***thiol*** group molar
ratios are
described herein. Alternatively, the hydroxy ***thiol***
ester
epoxide group to ***thiol*** group molar ratio can
be less
than 1.5; alternatively, less than 1.0; alternatively, less than
0.5;
alternatively, less than 0.25; or alternatively, less than 0.1.
In other
embodiments, the hydroxy ***thiol*** ester can be
substantially free
of ***epoxide*** groups.
DETD In another aspect, the process to produce hydroxy ***thiol***
ester
produces a hydroxy ***thiol*** ester wherein at least 20
percent of
the side chains comprise an .alpha.-hydroxy ***thiol***

group. Other hydroxy ***thiol*** ester embodiments wherein the hydroxy ***thiol*** ester contains a percentage of side chains comprising .alpha.-hydroxy ***thiol*** groups are described herein.

DETD Hydroxy ***Thiol*** Ester from a Polyol and a Hydroxy ***Thiol***
Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process to prepare the hydroxy ***thiol*** ester is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a hydroxy ***thiol*** containing carboxylic acid and/or ***thiol*** containing carboxylic acid derivative and reacting the polyol and hydroxy ***thiol*** containing carboxylic acid and/or hydroxy ***thiol*** containing carboxylic acid to form a hydroxy ***thiol*** ester composition. This process can be applied to any polyol, any hydroxy ***thiol*** containing carboxylic acid, or any ***thiol*** containing carboxylic acid derivative described herein. The process for producing the hydroxy ***thiol*** ester composition can also include any additional process steps or process conditions described herein. Additionally, the process for producing the hydroxy ***thiol*** ester composition can form any ***thiol*** ester described herein.

DETD In some embodiments, the hydroxy ***thiol*** ester composition includes hydroxy ***thiol*** ester molecules that have an average of at least 1 ester groups per hydroxy ***thiol*** ester molecule and an average of at least 1 .alpha.-hydroxy ***thiol*** groups per hydroxy ***thiol*** ester molecule.

DETD The polyol used to produce the hydroxy ***thiol*** ester by contacting a polyol and a hydroxy ***thiol*** carboxylic acid and/or hydroxy ***thiol*** carboxylic acid equivalent (for example a hydroxy ***thiol*** carboxylic acid methyl ester) can be any polyol or mixture of polyols that can produce the described ***thiol*** containing ester.

DETD In one aspect, the polyol used to produce the hydroxy ***thiol*** ester can comprise from 2 to 20 carbon atoms. In other embodiments, the polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7 carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments, the polyol may be a mixture of polyols having an average of 2 to 20 carbon atoms; alternatively, an average of from 2 to 10

carbon atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the hydroxy ***thiol*** ester can have any number of hydroxy groups needed to produce the hydroxy ***thiol*** ester as described herein. In some embodiments, the polyol has 2 hydroxy groups; alternatively 3 hydroxy groups; alternatively, 4 hydroxy groups; alternatively, 5 hydroxy groups; or alternatively, 6 hydroxy groups. In other embodiments, the polyol comprises at least 2 hydroxy groups; alternatively at least 3 hydroxy groups; alternatively, at least 4 hydroxy groups; or alternatively, at least 5 hydroxy groups; at least 6 hydroxy groups. In yet other embodiments, the polyol comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4 hydroxy groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the hydroxy ***thiol*** ester is a mixture of polyols. In an embodiment, the mixture of polyols has an average of at least 1.5 hydroxy groups per polyol molecule. In other embodiments, the mixture of polyols has an average of at least 2 hydroxy groups per polyol molecule; alternatively, an average of at least 2.5 hydroxy groups per polyol molecule; alternatively, an average of at least 3.0 hydroxy groups per polyol molecule; or alternatively, an average of at least 4 hydroxy groups per polyol molecule. In yet another embodiment, the mixture of polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule; alternatively, an average of 2 to 6 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol molecule; alternatively, an average of 3 to 4 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups per polyol molecule; or alternatively, an average of 2.5 to 4.5 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the hydroxy ***thiol*** ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD The hydroxy ***thiol*** carboxylic acid and/or hydroxy
 thiol carboxylic acid equivalent used to produce the
hydroxy ***thiol*** ester by contacting a polyol and a hydroxy
thiol
 carboxylic acid and/or hydroxy ***thiol*** carboxylic acid
 equivalent can be any hydroxy ***thiol*** carboxylic acid
mixture
 comprising hydroxy ***thiol*** carboxylic acids, hydroxy
 thiol carboxylic acid equivalent or mixture comprising
hydroxy ***thiol*** carboxylic acid equivalents that can produce the
described
 hydroxy ***thiol*** containing ester. When talking about the
 characteristics hydroxy ***thiol*** carboxylic acid
equivalent or
 hydroxy ***thiol*** carboxylic acid equivalents, properties
such as
 number of carbon atoms, average number of carbon atom, molecular
weight
 or average molecular weight, number of ***thiol*** group, and
 average number of ***thiol*** groups, one will understand the
these
 properties will apply to the portion of the ***thiol***
carboxylic
 acid equivalent which adds to the polyol to form the
thiol
 ester.

DETD In an aspect, the hydroxy ***thiol*** carboxylic acid and/or
 hydroxy ***thiol*** carboxylic acid equivalent used to
produce the
 thiol ester comprises from 2 to 28 carbon atoms. In an
embodiment, the hydroxy ***thiol*** carboxylic acid and/or
hydroxy ***thiol*** carboxylic acid equivalents comprises from 4 to
26 carbon
 atoms; alternatively, from 8 to 24 carbon atoms; alternatively,
from 12
 to 24 carbon atoms; or alternatively, from 14 to 20 carbon atoms.
In
 other embodiments, a mixture comprising hydroxy ***thiol***
 carboxylic acids and/or mixture comprising hydroxy ***thiol***
 carboxylic acid equivalents has an average of 2 to 28 carbon
atoms per
 carboxylic acid and/or carboxylic acid equivalent; alternatively,
from 4
 to 26 carbon per carboxylic acid and/or carboxylic acid
equivalent;
 alternatively, from 8 to 24 carbon atoms per carboxylic acid
and/or
 carboxylic acid equivalent; alternatively, from 12 to 24 carbon
atoms
 per carboxylic acid and/or carboxylic acid equivalent; or
alternatively,
 from 14 to 20 carbon atoms per carboxylic acid and/or carboxylic
acid
 equivalent.

DETD In another aspect, the hydroxy ***thiol*** carboxylic acid
and/or
 hydroxy ***thiol*** carboxylic acid equivalent used to

produce the
thiol ester has at least 1 ***thiol*** group,
alternatively
2 ***thiol*** groups. In some embodiments, a mixture
comprising
hydroxy ***thiol*** carboxylic acids and/or mixture
comprising
hydroxy ***thiol*** carboxylic acid equivalents has an
average of
from 0.5 to 3 ***thiol*** groups per carboxylic acid and/or
carboxylic acid equivalent; alternatively, an average of from 1
to 2
thiol groups per carboxylic acid and/or carboxylic acid
equivalent.
DETD In another aspect, the hydroxy ***thiol*** carboxylic acid
and/or
hydroxy ***thiol*** carboxylic acid equivalent used to
produce the
thiol ester has at least 1 hydroxy group;
alternatively, at
least 2 hydroxy groups. In some embodiments, a mixture comprising
hydroxy ***thiol*** carboxylic acids and/or mixture
comprising
hydroxy ***thiol*** carboxylic acid equivalents has an
average of
from 0.5 to 3 hydroxy groups per carboxylic acid and/or
carboxylic acid
equivalent; alternatively, an average of from 1 to 2 hydroxy
groups per
carboxylic acid and/or carboxylic acid equivalent.
DETD In another aspect, the hydroxy ***thiol*** carboxylic acid
and/or
hydroxy ***thiol*** carboxylic acid equivalent used to
produce the
hydroxy ***thiol*** ester has a molecular weight greater than
100;
alternatively greater than 180; alternatively greater than 240;
or
alternatively greater than 260. In other embodiments, the hydroxy
thiol carboxylic acid and/or hydroxy ***thiol***
carboxylic
acid equivalent has a molecular weight from 100 to 500;
alternatively,
from 120 to 420; alternatively, from 180 to 420; alternatively,
from 240
to 420; a mixture or alternatively, from 260 to 360. In some
embodiments, a mixture comprising hydroxy ***thiol***
carboxylic
acids and/or mixture comprising hydroxy ***thiol***
carboxylic acid
equivalents has an average molecular weight greater than 100 per
carboxylic acid and/or carboxylic acid equivalent; alternatively
greater
than 180 per carboxylic acid and/or carboxylic acid equivalent;
alternatively greater than 240 per carboxylic acid and/or
carboxylic
acid equivalent; or alternatively greater than 260 per carboxylic
acid
and/or carboxylic acid equivalent. In yet other embodiments, the
mixture

comprising hydroxy ***thiol*** carboxylic acid and/or mixture
 comprising hydroxy ***thiol*** carboxylic acid equivalents
 has an
 average molecular weight from 100 to 500 per carboxylic acid
 and/or
 carboxylic acid equivalent; alternatively, from 120 to 420 per
 carboxylic acid and/or carboxylic acid equivalent; alternatively,
 from
 180 to 420 per carboxylic acid and/or carboxylic acid equivalent;
 alternatively, from 240 to 420 per carboxylic acid and/or
 carboxylic
 acid equivalent; a mixture or alternatively, from 260 to 360 per
 carboxylic acid and/or carboxylic acid equivalent.
 DETD In some aspects, the reaction between the polyol and the hydroxy
 thiol containing carboxylic acid and/or hydroxy
 thiol
 containing carboxylic acid derivative occurs in the presence of a
 solvent. In other aspects, the reaction between the polyol and
 the
 hydroxy ***thiol*** containing carboxylic acid and/or hydroxy
 thiol containing carboxylic acid derivative occurs in
 the
 substantial absence of a solvent. In aspects wherein the reaction
 between the polyol and the hydroxy ***thiol*** containing
 carboxylic
 acid and/or hydroxy ***thiol*** containing carboxylic acid
 derivative occurs in the presence of a solvent, the solvent is
 selected
 from the group consisting of an aliphatic hydrocarbon, an ether,
 an
 aromatic compound, or any combination thereof. Generally, the
 solvent,
 regardless of its chemical class, includes from 1 to 20 carbon
 atoms;
 alternatively, from 3 to 10 carbon atoms. When the solvent
 includes the
 aliphatic hydrocarbon, the aliphatic hydrocarbon is butane,
 isobutane,
 pentane, hexane, heptane, octane, or any mixture thereof. When
 the
 solvent includes the aromatic compound, the aromatic compound is
 benzene, toluene, xylene, ethylbenzene, or any mixture thereof.
 When the
 solvent includes the ether, the ether is diethyl ether, dipropyl
 ether,
 tetrahydrofuran, and any mixture thereof.
 DETD When a solvent is used for the reaction between the polyol and
 the
 hydroxy ***thiol*** containing carboxylic acid and/or hydroxy
 thiol containing carboxylic acid derivative, the
 quantity of
 solvent can be any amount that facilitates the reaction. In some
 embodiments, the mass of the solvent is less than 30 times the
 mass of
 the hydroxy ***thiol*** containing carboxylic acid and/or
 hydroxy
 thiol containing carboxylic acid derivative. In other
 embodiments, the mass of the solvent is less than 20 times the
 mass of
 the hydroxy ***thiol*** ester; alternatively, less than 15

times the
 mass of the hydroxy ***thiol*** containing carboxylic acid
 and/or
 hydroxy ***thiol*** containing carboxylic acid derivative;
 alternatively, less than 10 times the mass of the hydroxy
 thiol
 containing carboxylic acid and/or hydroxy ***thiol***
 containing
 carboxylic acid derivative; or alternatively, less than 5 times
 the mass
 of the hydroxy ***thiol*** containing carboxylic acid and/or
 hydroxy
 thiol containing carboxylic acid derivative. In other
 embodiments, the mass of the solvent is from 2 times to 20 times
 the
 mass of the hydroxy ***thiol*** containing carboxylic acid
 and/or
 hydroxy ***thiol*** containing carboxylic acid derivative;
 alternatively, from 3 times to 15 times the mass of the hydroxy
 thiol containing carboxylic acid and/or hydroxy
 thiol
 containing carboxylic acid derivative; or alternatively, from 5
 times to
 10 times the mass of the hydroxy ***thiol*** containing
 carboxylic
 acid and/or hydroxy ***thiol*** containing carboxylic acid
 derivative.
 DETD The equivalents of hydroxy ***thiol*** containing carboxylic
 acid
 derivative and/or hydroxy ***thiol*** containing carboxylic
 acid
 derivative carboxylic acid groups to equivalents of polyol
 hydroxy
 groups molar ratio (hereinafter referred to as "carboxylic acid
 group to
 polyol hydroxy group molar ratio") utilized in the process to
 produce
 the hydroxy ***thiol*** ester can be any carboxylic acid
 group to
 polyol hydroxy group molar ratio that produces the desired
 hydroxy
 thiol ester. In some embodiments, the carboxylic acid
 group to
 polyol hydroxy group molar ratio is greater than 0.4. In other
 embodiments, the carboxylic acid group to polyol hydroxy group
 molar
 ratio is greater than 0.6; alternatively, greater than 0.8;
 alternatively, greater than 1; or alternatively, greater than
 1.1. In
 other embodiments, the carboxylic acid group to polyol hydroxy
 group
 molar ratio ranges from 0.4 to 1.3; alternatively, from 0.6 to
 1.2, or
 alternatively, from 0.8 to 1.1.
 DETD In some aspects, the reaction between the polyol and the hydroxy
 thiol containing carboxylic acid and/or hydroxy
 thiol
 containing carboxylic acid derivative is catalyzed. In some
 embodiments,
 the catalyst is a mineral acid, such as sulfuric or phosphoric

acid. In

other embodiments, the catalyst is an organic acid. In
embodiments, for
example, the organic acid is methane sulfonic acid or toluene
sulfonic
acid. Other suitable types of catalyst will be apparent to those
of
skill in the art and are to be considered within the scope of the
present invention.

DETD The reaction of the polyol and the hydroxy ***thiol***
containing
carboxylic acid and/or hydroxy ***thiol*** containing
carboxylic
acid derivative can occur in a batch reactor or a continuous
reactor, as
described herein. The reaction between the polyol and the hydroxy
thiol containing carboxylic acid and/or hydroxy
thiol
containing carboxylic acid derivative can be performed at any
temperature capable of forming the hydroxy ***thiol*** ester.

In
some embodiments, the polyol and the hydroxy ***thiol***
containing
carboxylic acid and/or hydroxy ***thiol*** containing
carboxylic
acid derivative can be reacted at a temperature greater than
20.degree.

C. In other embodiments, the polyol and the hydroxy ***thiol***
containing carboxylic acid and/or hydroxy ***thiol***
containing
carboxylic acid derivative can be reacted at a temperature
greater than
50.degree. C.; alternatively, greater than 75.degree. C.; or
alternatively, greater than 100.degree. C. In yet other
embodiments, the
polyol and the hydroxy ***thiol*** containing carboxylic acid
and/or
hydroxy ***thiol*** containing carboxylic acid derivative can
be
reacted at a temperature from 20.degree. C. to 250.degree. C.;
alternatively, from 50.degree. C. to 200.degree. C.;
alternatively, from
75.degree. C. to 175.degree. C.; or alternatively, from
100.degree. C.
to 150.degree..

DETD The time required for the reaction of the polyol and the hydroxy
thiol containing carboxylic acid and/or hydroxy
thiol

containing carboxylic acid derivative can be any time required to
form

the described hydroxy ***thiol*** ester composition.

Generally, the

reaction time is at least 5 minutes. In some embodiments, the
reaction
time is at least 30 minutes; alternatively, at least 1 hour; or
alternatively, at least 2 hours. In yet other embodiments, the
reaction

time ranges from 5 minutes to 72 hours; alternatively, from 30
minutes
to 48 hours; alternatively, from 1 hour minutes to 36 hours; or

alternatively, from 2 hours and 24 hours.

DETD The reaction between the polyol and the hydroxy ***thiol***
containing carboxylic acid and/or hydroxy ***thiol***
containing carboxylic acid derivative can be performed at any reaction
pressure that maintains the polyol and the hydroxy ***thiol***
containing carboxylic acid and/or hydroxy ***thiol*** containing
carboxylic acid derivative in a liquid state. In some embodiments, the
reaction pressure ranges from 0 psia to 2000 psia. In other embodiments,
the reaction pressure ranges from 0 psia to 1000 psia; alternatively,
from 0 psia and 500 psia; or alternatively, from 0 psia to 300 psia.

DETD In some embodiments, the process to produce the hydroxy
thiol ester composition by reacting a polyol and the hydroxy
thiol containing carboxylic acid and/or hydroxy ***thiol***
containing carboxylic acid derivative can further include a step to remove
excess or residual polyol, hydroxy ***thiol*** containing carboxylic
acid, and/or hydroxy ***thiol*** containing carboxylic acid
derivative once the polyol has reacted with the hydroxy ***thiol***
containing carboxylic acid or hydroxy ***thiol*** containing carboxylic
acid derivative. In some embodiments, the ***thiol*** ester is
vacuum stripped. In some embodiments, the hydroxy ***thiol*** ester
is vacuum stripped at a temperature between 25.degree. C. and
250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In
other embodiments, the hydroxy ***thiol*** ester is sparged with an
inert gas to remove excess polyol, hydroxy ***thiol*** containing
carboxylic acid, and/or hydroxy ***thiol*** containing
carboxylic acid derivative. In some embodiments, the hydroxy ***thiol***
ester is sparged with an inert gas at a temperature between 25.degree.
C. and 250.degree. C., or alternatively, between 50.degree. C. and
200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the
stripped or sparged hydroxy ***thiol*** ester oil comprises less than
5 excess polyol, hydroxy ***thiol*** containing carboxylic
acid, or hydroxy ***thiol*** containing carboxylic acid derivative. In
other

embodiments, the stripped or sparged hydroxy ***thiol*** ester oil comprises less than 2 weight percent excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative; less than 1 weight percent excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative; or alternatively, less than 0.5 weight percent excess polyol, hydroxy ***thiol*** containing carboxylic acid, and/or hydroxy ***thiol*** containing carboxylic acid derivative.

DETD A method of making a thioacrylate containing ester composition is advantageously provided as another embodiment of the present invention.

The process for producing the thioacrylate containing ester comprising contacting a ***thiol*** ester with an acrylate and converting at least one ***thiol*** group to a ***thiol*** acrylate group. The process can be applied to any of the ***thiol*** esters described herein and used to any thioacrylate ester described herein. The process for producing the thioacrylate ester can also include any additional process steps or process conditions described herein.

DETD The acrylate compound can be any acrylate compound capable of reacting with a ***thiol*** group to form the ***thiol*** acrylate group.

In some embodiments, the acrylate compound can be an acrylic halide. In other embodiments, the acrylate compound can be an acrylic acid. In yet other embodiments, the acrylate compound can be an acrylic anhydride.

DETD In some aspects, the conversion of the ***thiol*** group to a thioacrylate group occurs in the presence of a solvent. In other aspects the conversion of the ***thiol*** group to a thioacrylate group occurs in the substantial absence of a solvent. In aspects wherein the conversion of the ***thiol*** group to a thioacrylate group occurs in the presence of a solvent, the solvent may be an aliphatic hydrocarbon, an ether, and aromatic compound. Generally, the solvent, regardless of its chemical class, includes from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane,

isobutane,
pentane, hexane, heptane, octane, or any mixture thereof. When
the solvent includes the aromatic compound, the aromatic compound is
benzene, toluene, xylene, ethylbenzene, or any mixture thereof.
When the solvent includes the ether, the ether is diethyl ether, dipropyl
ether,
tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the conversion of the ***thiol***
group to a thioacrylate group, the quantity of solvent can be any
amount that facilitates the reaction. In some embodiments, the mass of the
solvent is less than 30 times the mass of the ***thiol*** ester. In
other
embodiments, the mass of the solvent is less than 20 times the
mass of the ***thiol*** ester; alternatively, less than 15 times the
mass of the ***thiol*** ester; alternatively, less than 10 times the
mass of the ***thiol*** ester; or alternatively, less than 5 times
the mass of the ***thiol*** ester. In other embodiments, the mass of
the solvent is from 2 times to 20 times the mass of the ***thiol***
ester; alternatively, from 3 times to 15 times the mass of the
thiol ester; alternatively, 4 times to 15 times the
mass of the ***thiol*** ester; or alternatively, from 5 times to 10 times
the mass of the ***thiol*** ester.

DETD In some aspects the conversion of the ***thiol*** group to
the thioacrylate group occurs in the presence of a catalyst. In some
embodiments, the catalyst is homogeneous. In some embodiments,
the catalyst is an organic amine. Examples of suitable organic amines
include triethylamine, tripropylamine, tributylamine, and
pyridine. In other embodiments, the catalyst is heterogeneous. Examples of
suitable catalysts include Amberlyst A-21 and Amberlyst A-26. Other
suitable catalysts will be apparent to those of skill in the art and are
to be considered within the scope of the present invention.

DETD The conversion of the ***thiol*** group to a thioacrylate
group can be performed at any conversion temperature that is capable of
converting the ***thiol*** group to a thioacrylate group. In some
embodiments, the conversion temperature is greater than -20.degree. C. In
other
embodiments, the conversion temperature is greater than 0.degree.
C.; alternatively, greater than 20.degree. C.; alternatively, greater

than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the conversion temperature ranges from -20.degree. C. to 250.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 50.degree. C. to 150.degree. C.

DETD The conversion time required for the conversion of the ***thiol*** group to a thioacrylate group can be any time required to form the described thioacrylate containing ester. Generally, the conversion time is at least 5 minutes. In some embodiments, the conversion time is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour. In other embodiments, the conversion time ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; or alternatively, from 45 minutes to 3 hours.

DETD The conversion of the ***thiol*** group to a thioacrylate group can be performed at any conversion pressure that maintains the ***thiol*** ester and the acrylate compound in the liquid state. In some embodiments, the conversion pressure ranges from 0 psia to 2000 psia. In other embodiments, the conversion pressure ranges from 0 psia to 1000 psia; or alternatively, from 0 psia to 500 psia.

DETD Process for Producing Cross-Linked ***Thiol*** Ester

DETD As an embodiment of the present invention, a process for producing a cross-linked ***thiol*** ester composition is advantageously provided. Minimally, in some embodiments, the process to produce the cross-linked ***thiol*** ester composition comprises contacting a ***thiol*** ester composition with an oxidizing agent and reacting the ***thiol*** ester composition and an oxidizing agent to form the ***thiol*** ester oligomer having at least two ***thiol*** ester monomers connected by a polysulfide linkage having the structure --S.sub.Q--, wherein Q is an integer greater than 1. The disclosed method may be applied to any ***thiol*** ester described herein to produce any cross-linked ***thiol*** ester composition as described herein. The process to produce the cross-linked ***thiol*** ester composition can also include any additional process steps or process

conditions as described herein.

DETD When elemental sulfur is used as the oxidizing agent, the quantity of elemental sulfur utilized to form the cross-linked ***thiol*** ester composition is determined as a function of the ***thiol*** sulfur content of the ***thiol*** ester composition. In an aspect, the weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester composition is at least 0.5. In some embodiments, the weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester composition is at least 5; alternatively, at least 10, alternatively, at least 15, or alternatively, at least 20. In other embodiments, the weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester composition ranges from 0.5 to 32; alternatively, ranges from 1 to 24; alternatively, ranges from 2 to 16; or alternatively, ranges from 3 to 10.

DETD In an aspect, the reaction of the ***thiol*** ester and elemental sulfur occurs in the presence of a catalyst. The catalyst can be any catalyst that catalyzes the formation of the polysulfide linkage between at least two ***thiol*** ester monomers. In some embodiments, the catalyst is an amine. In further embodiments, the catalyst is a tertiary amine.

DETD The formation of the cross-linked ***thiol*** ester can occur in a batch reactor or a continuous reactor, as described herein. The formation of the cross-linked ***thiol*** ester can occur at any temperature capable of forming the ***thiol*** ester. In some embodiments, the formation of the cross-linked ***thiol*** ester can occur at a temperature greater than 25.degree. C. In other embodiments, the formation of the cross-linked ***thiol*** ester can occur at a temperature greater than 50.degree. C.; alternatively, greater than 70.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the formation of the cross-linked ***thiol*** ester occurs at a temperature from 25.degree. C. to 150.degree. C.; alternatively, from 50.degree. C. to 150.degree. C.; alternatively, from 70.degree. C. to 120.degree. C.; or alternatively, from 80.degree. C. to 110.degree. C.

DETD The time required to form the cross-linked ***thiol*** ester can be

any time required to form the desired cross-linked ***thiol*** ester. Generally, the time required to form the cross-linked ***thiol*** ester is at least 15 minutes. In some

embodiments, the

time required to form the cross-linked ***thiol*** ester is at least

30 minutes; alternatively, at least 1 hour; or alternatively, at least 2

hours. In yet other embodiments, the time required to form the cross-linked ***thiol*** ester ranges from 15 minutes to 72

hours;

alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour

minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD In embodiments, the process to produce the cross-linked ***thiol***

ester further comprises a step to remove residual hydrogen sulfide. In

some embodiments the cross-linked ***thiol*** ester is vacuum stripped. In some embodiments, the cross-linked ***thiol***

ester is

vacuum striped at a temperature between 25.degree. C. and 250.degree.

C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, 75 and 150.degree. C. In some embodiments, the

cross-linked ***thiol*** ester oil is sparged with an inert gas to

remove residual hydrogen sulfide. In other embodiments, the cross-linked

thiol ester is sparged with an inert gas at a temperature

between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, between 75

and

150.degree. C. In yet other embodiments, the vacuum stripping is performed while sparging the cross-linked ***thiol*** ester

with an

inert gas. In yet other embodiments, the vacuum stripping is performed

while sparging the cross-linked ***thiol*** ester an inert gas at a

temperature between 25.degree. C. and 250.degree. C.;

alternatively,

between 50.degree. C. and 200.degree. C.; or alternatively, 75 and

150.degree. C. In some embodiments, the inert gas is nitrogen.

DETD Generally, the stripped or sparged cross-linked ***thiol*** ester

comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged ***thiol*** -containing

ester

oil comprises less than 0.05 weight percent hydrogen sulfide; alternatively, less than 0.025 weight percent hydrogen sulfide;

or

alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The present invention advantageously provides processes for producing

sulfide-containing esters as embodiments of the present

invention.

Generally, the sulfide-containing esters can be prepared by two processes. As an embodiment of the present invention, the first process used to produce a sulfide-containing ester comprises contacting an unsaturated ester and a ***mercaptan*** and reacting the ester and ***mercaptan*** to form a sulfide-containing ester.

As another embodiment of the present invention, the second process used to produce a sulfide-containing ester comprises contacting an epoxidized unsaturated ester and a ***mercaptan*** sulfide and reacting the unsaturated ester and ***mercaptan*** to form a sulfide-containing ester. Additional aspects of the two sulfide-containing ester production processes are described below.

DETD The sulfide-containing esters and sulfide-containing ester compositions described herein can be produced by a process comprising contacting a ***mercaptan*** and an unsaturated ester and reacting the ***mercaptan*** and the unsaturated ester to form a sulfide-containing ester. The process can be applied to any of the unsaturated esters and ***mercaptans*** described herein. The process for producing the sulfide-containing ester can also include any additional process steps or process conditions described herein. Additionally, the process for producing the sulfide-containing ester can form any sulfide-containing ester described herein.

DETD In some aspects, the reaction between the ***mercaptan*** and the unsaturated ester occurs in the presence of a solvent. In other aspects the reaction between the ***mercaptan*** and the unsaturated ester occurs in the substantial absence of a solvent. When the reaction occurs in the presence of a solvent, the solvent is selected from an aliphatic hydrocarbon, an ether, an aromatic compound, an alcohol, or any combination thereof. Generally, the solvent, regardless of its chemical class, can comprise from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms. When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes an aromatic

compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes an alcohol, the alcohol is methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, or any mixture thereof. When the solvent includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the ***mercaptan*** and the unsaturated ester, the quantity of solvent can be any amount that facilitates the reaction, as understood by those of skill in the art. In some embodiments, the mass of the solvent is less than 30 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester; alternatively, less than 15 times the mass of the unsaturated ester; alternatively, less than 10 times the mass of the unsaturated ester; or alternatively, less than 5 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the unsaturated ester; alternatively, from 3 times to 15 times the mass of the unsaturated ester; alternatively, from 4 times to 15 times the mass of the unsaturated ester; or alternatively, from 5 times to 10 times the mass of the unsaturated ester.

DETD The molar ratio of ***mercaptan*** to molar equivalents of unsaturated ester carbon-carbon double bonds (herein after "***mercaptan*** to carbon-carbon double bond molar ratio") utilized in the process to produce the sulfide-containing ester can be any ***mercaptan*** to carbon-carbon double bond molar ratio that produces the desired sulfide-containing ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the equation: $\frac{UES\ C.dbd.C}{UES\ GMW}$ In this equation, UES GMW is the average gram molecular weight of the unsaturated ester, UES Mass is the mass of the unsaturated ester, and UES C.dbd.C is the average number of double bonds per unsaturated ester molecule. In some embodiments, the ***mercaptan*** to carbon-carbon double bond molar ratio is greater than 0.25. In other embodiments, the ***mercaptan*** to carbon-carbon double bond molar ratio is greater than 0.5; alternatively, greater than 0.75; alternatively, greater than 1; alternatively, greater than 1.25; or alternatively, greater than 1.5. In other embodiments, the ***mercaptan*** to carbon-carbon double bond

molar ratio can range from 0.25 to 2; alternatively, from 0.5 to 1.5, or alternatively, from 0.75 to 1.25.

DETD In some aspects the reaction between the ***mercaptan*** and the unsaturated ester is catalyzed. The reaction of the ***mercaptan*** and the unsaturated ester can be catalyzed by a heterogeneous catalyst or homogeneous catalyst, as described herein. In some aspects, the reaction between the ***mercaptan*** and the unsaturated ester is initiated by a free radical initiator or ultraviolet radiation, as described herein.

DETD The free radical initiator can be any free radical initiator capable of forming free radicals under thermal or light photolysis. Generally, the free radical initiator is selected from the general class of compounds having a --N.dbd.N-- group or a --O-- O-- group. Specific classes of free radical initiators include diazo compounds, dialkyl peroxides, hydroperoxides, and peroxy esters. Specific initiators include azobenzene, 2,2'-azobis(2-methylpropionitrile, 4,4'-azobis(4-cyanovaleric acid), 1,1'-azobis(cyclohexanecarbonitrile), 2,2'-azobis(2methylpropane), 2,2'-azobis(2-methylpropionamidine) dihydrochloride, methylpropionitrile, azodicarboxamide, tert-butyl hydroperoxide, di-tert-butyl peroxide, octylperbenzoate. In some embodiments, the free radical initiated reaction of the ***mercaptan*** and the unsaturated ester is performed at a reaction temperature within ± 50 degree. C. of the 1 hour half life of the free radical initiator. In other embodiments, the reaction temperature is within ± 25 degree. C. of the 1 hour half life of the free radical initiator; alternatively, the reaction temperature is within ± 20 degree. C. of the 1 hour half life of the free radical initiator; alternatively, the reaction temperature is within ± 15 degree. C. of the 1 hour half life of the free radical initiator; or alternatively, the reaction temperature is within ± 10 degree. C. of the 1 hour half life of the free radical initiator. In embodiments where the free radical initiated reaction of the ***mercaptan*** and the unsaturated ester is initiated by light photolysis, the light can be any light capable creating free radicals. In some embodiments, the light is UV radiation. Other sources of light capable of creating free radicals

will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In another aspect, the reaction of the ***mercaptan*** and the unsaturated ester is initiated by UV radiation. In these embodiments, the UV radiation may be any UV radiation capable of initiating the reaction of the ***mercaptan*** and the unsaturated ester. In some embodiments, the UV radiation is generated by a medium pressure mercury lamp.

DETD The reaction of the ***mercaptan*** and the unsaturated ester can occur in a batch reactor or a continuous reactor. Any of the batch or continuous reactors described herein can be used in this reaction. Other suitable reactors will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction time for reacting the ***mercaptan*** and the unsaturated ester can be any time required to form the sulfide-containing ester. Generally, the reaction time is at least 5 minutes. In some embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15 minutes to 36 hours.

DETD In some embodiments, the process to produce the sulfide-containing ester further comprises a step to remove any residual ***mercaptan*** that remains after reacting the ***mercaptan*** and the unsaturated ester. In some embodiments, the sulfide-containing ester is vacuum stripped to remove the residual ***mercaptan***. In some embodiments, the sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the sulfide-containing ester is sparged with an inert gas to remove the residual ***mercaptan***. In some embodiments, the sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged sulfide-containing ester comprises less than 5 weight percent of the ***mercaptan***. In other embodiments, the stripped or sparged sulfide-containing

ester comprises less than 2 weight percent of the ***mercaptan*** ; alternatively, less than 1 weight percent of the ***mercaptan*** ; or alternatively, less than 0.5 weight percent of the ***mercaptan*** .

DETD The reaction between the ***mercaptan*** and the unsaturated ester can be performed at any temperature capable of forming the sulfide-containing ester. In some embodiments, the ***mercaptan*** and the unsaturated ester can be reacted at a reaction temperature of greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the ***mercaptan*** and the unsaturated ester can be reacted at a temperature from -20.degree. C. to 250.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 80.degree. C. to 160.degree. C.

DETD The reaction between the ***mercaptan*** and the unsaturated ester can be performed at any pressure that maintains the ***mercaptan*** and the unsaturated ester in a substantially liquid state. In some embodiments, the ***mercaptan*** and the unsaturated ester can be performed at a reaction pressure ranging from 0 psig to 2000 psig. In other embodiments, the reaction pressure ranges from 0 psig to 1000 psig; alternatively, from 0 psig to 500 psig; or alternatively, from 0 psig to 200 psig.

DETD Using the disclosed process, sulfide-containing ester having a low carbon-carbon double bond to sulfide group molar ratio can be produced. In an aspect, the process for producing the sulfide-containing ester forms a sulfide-containing ester having a carbon-carbon double bond to ***thiol*** group molar ratio of less than 1.5. Additional carbon-carbon double bond to sulfide group molar ratios are disclosed herein.

DETD As another embodiment of the present invention, another process for producing a class of sulfide-containing esters, which includes hydroxy sulfide-containing esters, is advantageously provided. In this embodiment, the hydroxy sulfide-containing esters and hydroxy sulfide-containing ester compositions can be produced by a

process

comprising the steps of contacting a ***mercaptan*** and an epoxidized unsaturated ester and reacting the ***mercaptan***

and

the epoxidized unsaturated ester to produce or form the hydroxy sulfide-containing ester. The process can be applied to any ***mercaptan*** and/or any epoxidized unsaturated esters

described

herein. The process for producing the hydroxy sulfide-containing ester

ester

can also include any additional process steps or process

conditions as

described herein. Additionally, the process for producing the

hydroxy

sulfide-containing ester can form any hydroxy sulfide-containing

ester

as described herein.

DETD In some aspects, the reaction between the ***mercaptan***

and the

unsaturated ester occurs in the presence of a solvent. In other

aspects

the reaction between the ***mercaptan*** and the unsaturated

ester

occurs in the substantial absence of a solvent. When the reaction

occurs

in the presence of a solvent, the solvent is selected from an

aliphatic

hydrocarbon, an ether, an aromatic compound, or any combination

thereof.

Generally, the solvent, regardless of its chemical class, can

comprise

from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon

atoms.

When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane,

octane, or

any mixture thereof. When the solvent includes an aromatic

compound, the

aromatic compound is benzene, toluene, xylene, ethylbenzene, or

any

mixture thereof. When the solvent includes an ether, the ether is

diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture

thereof.

DETD When a solvent is used for the reaction between the

mercaptan

and the epoxidized unsaturated ester, the quantity of solvent can

be any

amount that facilitates the reaction, as understood by those of

skill in

the art. In some embodiments, the mass of the solvent is less

than 30

times the mass of the epoxidized unsaturated ester. In other

embodiments, the mass of the solvent is less than 20 times the

mass of

the epoxidized unsaturated ester; alternatively, less than 15

times the

mass of the epoxidized unsaturated ester; alternatively, less

than 10

times the mass of the epoxidized unsaturated ester; or

alternatively,

less than 5 times the mass of the epoxidized unsaturated ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the epoxidized unsaturated ester; alternatively, from 3 times to 15 times the mass of the epoxidized unsaturated ester; alternatively, from 4 times to 15 times the mass of the epoxidized unsaturated ester; or alternatively, from 5 times to 10 times the mass of the epoxidized unsaturated ester.

DETD The reaction of the ***mercaptan*** and the epoxidized unsaturated ester can occur using any ***mercaptan*** to molar equivalents of ***epoxide*** groups in the epoxidized unsaturated ester (hereinafter referred to as " ***mercaptan*** to ***epoxide*** group molar ratio") that is capable of producing the herein described .alpha.-hydroxy ***thiol*** esters. The molar equivalents of epoxidized unsaturated ester epoxidized groups can be calculated by the equation: ##EQU4##

DETD In this equation, EUES GMW is the average gram molecular weight of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES ***Epoxide*** is the average number of ***epoxide*** groups per epoxidized unsaturated ester molecule. In some embodiments, the ***mercaptan*** to ***epoxide*** group molar ratio is greater than 0.2. In other embodiments, the ***mercaptan*** to ***epoxide*** group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to ***epoxide*** group molar ratio ranges from 0.2 to 10; alternatively, from 0.5 to 8; alternatively, from 0.75 to 5; or alternatively, from 1 to 3.

DETD In some aspects, the reaction of the ***mercaptan*** and the epoxidized unsaturated ester occurs in the presence of a catalyst. Generally, the catalyst is any catalyst that is capable of catalyzing the reaction of the ***mercaptan*** and the epoxidized unsaturated ester to produce the desired hydroxy ***thiol*** ester. In one aspect, the catalyst is selected from the group consisting of homogeneous and heterogeneous catalysts. In other aspects, the catalyst is selected from the group consisting of zeolites, heterogeneous catalysts, homogeneous catalysts, and mixtures thereof. In another

aspect, the catalyst is an amine. In other aspects, the catalyst is selected from the group consisting of cyclic conjugated amines, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-ene, and mixtures thereof.

DETD In some aspects, the reaction of the ***mercaptan*** and the epoxidized unsaturated ester occurs in the presence of a catalyst. Generally, the catalyst is any catalyst that is capable of catalyzing the reaction of the ***mercaptan*** and the epoxidized unsaturated ester to produce the desired hydroxy ***thiol*** ester. In some embodiments the catalyst is an organic base. In some embodiments, the catalyst can be 1,8-diazabicyclo[5.4.0]undec-7-ene. (What other catalysts may be used?)

DETD The reaction of the ***mercaptan*** and the epoxidized unsaturated ester can occur in a batch reactor or a continuous reactor. Any of the batch or continuous reactors described herein can be used in this reaction. Other suitable reactors will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The time required for the reaction of the ***mercaptan*** and the epoxidized unsaturated ester can be any reaction time required to form the described hydroxy sulfide-containing ester. Generally, the reaction time is at least 15 minutes. In some embodiments, the reaction ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; or alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the process to produce the hydroxy sulfide-containing ester further comprises a step to remove the residual ***mercaptan*** after reacting the ***mercaptan*** and the epoxidized unsaturated ester. In some embodiments the hydroxy sulfide-containing ester is vacuum stripped. In some embodiments, the hydroxy sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy sulfide-containing ester is sparged with an inert gas to remove the ***mercaptan***. In some embodiments, the hydroxy sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C.

and
200.degree. C. In some aspects, the inert gas is nitrogen.
Generally,
the stripped or sparged hydroxy sulfide-containing ester
comprises less
than 5 weight percent of the ***mercaptan*** . In other
embodiments,
the stripped or sparged hydroxy sulfide-containing ester
comprises less
than 2 weight percent of the ***mercaptan*** ; alternatively,
less
than 1 weight percent of the ***mercaptan*** ; or
alternatively, less
than 0.5 weight percent of the ***mercaptan*** .
DETD The reaction between the ***mercaptan*** and the epoxidized
unsaturated ester can be performed at any reaction temperature
capable
of forming the hydroxy sulfide-containing ester. In some
embodiments,
the reaction temperature is greater than -20.degree. C. In other
embodiments, the reaction temperature is greater than 0.degree.
C.;
alternatively, greater than 20.degree. C.; alternatively, greater
than
50.degree. C.; or alternatively, greater than 80.degree. C. In
yet other
embodiments, the reaction temperature ranges from -20.degree. C.
to
200.degree. C.; alternatively, from 20.degree. C. to 170.degree.
C.; or
alternatively, from 80.degree. C. to 140.degree. C.
DETD The reaction between the ***mercaptan*** and the epoxidized
unsaturated ester can be performed at any reaction pressure that
maintains the ***mercaptan*** and the epoxidized unsaturated
ester
in a substantially liquid state. In some embodiments, the
reaction
pressure ranges from 0 psig to 2000 psig. In other embodiments,
the
reaction pressure ranges from 0 psig to 1000 psig; alternatively,
from 0
psig to 500 psig; or alternatively, from 0 psig to 200 psig.
DETD In another aspect, the process to produce a hydroxy sulfide-
containing
ester produces a hydroxy sulfide-containing ester having an
epoxide group to sulfide group molar ratio less than 2.
Other
hydroxy sulfide-containing ester ***epoxide*** group to
sulfide
group molar ratios are described herein. (The next passage needs
to be
incorporated into the hydroxy ***thiol*** ester section along
with
the first sentence of this paragraph.) Alternatively, the hydroxy
sulfide-containing ester ***epoxide*** group to ***thiol***
group molar ratio can be less than 1.5; alternatively, less than
1.0;
alternatively, less than 0.5, alternatively, less than 0.25; or
alternatively, less than 0.1. In other embodiments, the hydroxy
sulfide-containing ester can be substantially free of

epoxide

groups.

DETD As an embodiment of the present invention, processes for producing a

sulfonic acid-containing ester and for producing a sulfonate-containing

ester are advantageously provided. Generally, the process for producing

the sulfonic acid-containing ester comprises the steps of contacting a

thiol ester and an oxidizing agent and oxidizing at least one

thiol group of the ***thiol*** ester to produce a sulfonic

acid group. The process for producing the sulfonate-containing ester

comprises the steps of contacting a sulfonic acid-containing ester with

a base and forming a sulfonate-containing ester.

DETD In an embodiment, the process to prepare a sulfonic acid-containing

ester comprises the steps of contacting the ***thiol*** ester and

the oxidizing agent and oxidizing the ***thiol*** ester to produce

the sulfonic acid-containing ester. Generally the oxidizing agent oxidizes at least one

thiol group of the ***thiol*** ester to a sulfonate group. The process to produce the sulfonic

acid-containing ester composition can be applied to any ***thiol***

ester described herein to prepare any sulfonic acid-containing ester

described herein. In some embodiments, the ***thiol*** ester includes a hydroxy group. For example, the ***thiol*** ester

can be any hydroxy ***thiol*** ester described herein. The oxidizing agent

can be any oxidizing agent described herein.

DETD In some aspects, the oxidation of the ***thiol*** ester occurs in

the presence of a solvent. In some aspects, the solvent is water.

DETD The oxidizing agent that is contacted with the ***thiol*** ester

can be any oxidizing agent capable of oxidizing a ***thiol*** group

to a sulfonic acid group. In some embodiments, the oxidizing agent is

oxygen. In other embodiments, the oxidizing agent is chlorine. In other

embodiments, the oxidizing agent is dimethyl sulfoxide. In yet other

embodiments, the oxidizing agent is a combination of a hydrogen halide

and a catalytic amount of a dialkyl sulfide, such as dimethyl sulfoxide.

Other suitable oxidizing agents will be apparent to those of skill in

the art and are to be considered within the scope of the present invention.

DETD The oxidation of the ***thiol*** ester can be performed at any temperature capable of converting the ***thiol*** ester to a sulfonic acid-containing ester. In some embodiments, the ***thiol*** ester is oxidized at a temperature greater than -20.degree. C. In other embodiments, the ***thiol*** ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively, greater than 50.degree. C.

DETD The time required for the oxidation of the ***thiol*** ester can be any time required to form the desired sulfonic acid-containing ester. Generally, the time required for the oxidation of the ***thiol*** ester is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour. In some embodiments, the time required for the oxidation of the ***thiol*** ester ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; alternatively, from 45 minutes to 3 hours.

DETD The oxidation of the ***thiol*** ester can be performed at any pressure that maintains the ***thiol*** ester and the oxidation agent in the proper state, which is not always a liquid state, to oxidize the ***thiol*** ester to a sulfonic acid-containing ester. For example, when the oxidation agent is chlorine, the chlorine can be in the gaseous state. In some embodiments, the oxidation of the ***thiol*** ester can be performed at a pressure ranging from 0 to 2000 psig. In other embodiments, the oxidation of the ***thiol*** ester can be performed at a pressure ranging from 0 to 1000 psig; or alternatively, 0 to 500 psig.

DETD The oxidation of the ***thiol*** ester can be performed in a batch reactor or a continuous reactor, as described herein. Additionally, the process to produce the sulfonic acid-containing ester can comprise additional process steps as recognized by those skilled in the art.

DETD The formation of the sulfonate-containing ester can be performed at any temperature capable of converting the sulfonic acid group of the sulfonic acid-containing ester to a sulfonate group. In some embodiments, the sulfonate-containing ester is formed at a temperature greater than -20.degree. C. In other embodiments, the ***thiol*** ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively,

greater than 50.degree. C. In yet other embodiments, the ***thiol*** ester is oxidized at a temperature ranging from 0.degree. C. to 250.degree. C.; alternatively, from 0.degree. C. to 150.degree. C.; or alternatively, from 20.degree. C. to 100.degree. C.

DETD A preferred sulfur-containing vegetable oil is MVO available from Chevron Phillips Chemical Co. under the tradename Polymercaptan 358. Polymercaptan 358 is made by the free radical addition of hydrogen sulfide to the double bonds in soybean oil. Typically, Polymercaptan 358 has a ***thiol*** sulfur content of 5 to 10% and equivalent weights of 640 to 320, respectively.

DETD Another preferred sulfur-containing vegetable oil useful as part of the isocyanate-reactive component is a MHVO such as mercapto-hydroxy soybean oil. As described herein, a preferred mercapto-hydroxy soybean oil is made by the free radical addition of hydrogen sulfide to epoxidized soybean oil. Typically, the mercapto and hydroxy functionalities are equal and the ***mercaptan*** content is about 8.3% ***thiol*** sulfur. The equivalent weight of this material is 192, which includes both mercapto and hydroxy functionalities.

DETD Yet another preferred sulfur-containing vegetable oil useful as part of the isocyanate-reactive component is a CMVO such as sulfur cross-linked mercaptanized soybean oil. Sulfur cross-linked mercaptanized soybean oil is made by the addition of elemental sulfur to mercaptanized soybean oil. In this process, a portion of the ***mercaptan*** groups are consumed as cross-linking sites for the sulfur. Typical sulfur cross-linked mercaptanized soybean oil products by Chevron Phillips Chemical Co. include Runs #22, 194, 195, 196 and 197 and have a ***thiol*** sulfur content ranging from about 8.0% to 1.4% and equivalent weights ranging from about 400 to about 2250, respectively.

DETD For epoxy polymer encapsulated CRF material made from sulfur-containing vegetable oil, it has been found that the use of a tertiary amine catalyst is highly preferred. The amount used is such to be sufficient to give the desired reaction rate for the production of the encapsulated slow release fertilizer product. A non-limiting example of a suitable

amine catalyst is diazobicycloundecacene also known as
1,8-diazabicyclo[5,4,0]undec-7-ene [CAS# ***6674-22-2***] or
"DBU",
which is preferably used in the range of about 0.1% to 0.5% by
weight of
the coating. Other suitable catalyst materials will be apparent
to those
of ordinary skill in the art.

DETD The preferred sulfur-containing vegetable oil to be used in
production
of an epoxy polymer coated CRF material is MHVO such as mercapto-
hydroxy
soybean oil. One such material is mercapto-hydroxy soybean oil
known as
MHSO 566-84 produced by Chevron Phillips Chemical Co. This
preferred
material contains 8.33% ***thiol*** sulfur, with an
equivalent
weight of 384, based upon the ***mercaptan*** functionality.

DETD The unsaturated ester used as a feedstock to produce the
thiol
ester compositions described herein can be described using a
number of
different methods. One method of describing the unsaturated ester
feedstock is by the number of ester groups and the number of
carbon-carbon double bonds that comprise each unsaturated ester
oil
molecule. Suitable unsaturated ester used as a feedstock to
produce the
thiol ester compositions described herein minimally
comprise at
least 1 ester group and at least 1 carbon-carbon double bond.
However,
beyond this requirement, the number of ester groups and carbon-
carbon
double bonds comprising the unsaturated esters are independent
elements
and can be varied independently of each other. Thus, the
unsaturated
esters can have any combination of the number of ester groups and
the
number of carbon-carbon double bonds described separately herein.
Suitable, unsaturated esters can also contain additional
functional
groups such as alcohol, aldehyde, ketone, epoxy, ether, aromatic
groups,
and combinations thereof. As an example, the unsaturated esters
can also
comprise hydroxy groups. An example of an unsaturated ester that
contains hydroxy groups is castor oil. Other suitable unsaturated
esters
will be apparent to those of skill in the art and are to be
considered
within the scope of the present invention.

DETD In yet another aspect, the polyol or mixture of polyols used to
produce
the unsaturated ***thiol*** ester has a molecular weight or
average
molecular weight less than 500. In other embodiments, the polyol
or

mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD In some embodiments, suitable polyols include 1,2-ethanediol, 1,3-propanediol, 1,4-*****butanediol*****, 1,5-pentanediol, 1,6-hexanediol, dimethylolpropane, neopentylpropane, 2-propyl-2-ethyl-1,3-propanediol, 1,2-propanediol, 1,3-*****butanediol*****, diethylene glycol, triethylene glycol, polyethylene glycol, dipropylene glycol, tripropylene glycol, and polypropylene glycol; cyclohexanedimethanol, 1,3-dioxane-5,5-dimethanol; and 1,4-xylylenedimethanol and 1-phenyl-1,2-ethanediol, trimethylolpropane, trimethylolethane, trimethylolbutane, glycerol, 1,2,5-hexanetriol, pentaerythritol, ditrimethylolpropane, diglycerol, ditrimethylolethane, 1,3,5-trihydroxybenzene, 1,4-xylylenedimethanol, and 1-phenyl-1,2-ethanediol, or any combination thereof. In further embodiments, the polyol is glycerol, pentaerythritol, or mixtures thereof. In other embodiments, the polyol is glycerol, or alternatively pentaerythritol.

DETD Specific carboxylic acids used as a component of the carboxylic acid composition used to produce the unsaturated ester oil can have from 3 to 30 carbon atoms per carboxylic acid molecule. In some embodiments the carboxylic acid is linear. In some embodiments the carboxylic acid is branched. In some embodiments the carboxylic acid is a mixture of linear and branched carboxylic acids. In some embodiments the carboxylic acid can also comprise additional functional groups including alcohols, aldehydes, ketones, and *****epoxides*****, among others.

DETD Minimally, the epoxidized unsaturated ester comprises at least one *****epoxide***** group. In an embodiment the epoxidized unsaturated ester comprises at least 2 *****epoxide***** groups; alternatively, at least 3 *****epoxide***** groups; or alternatively, at least 4 *****epoxide*****.

In other embodiments, the epoxidized unsaturated ester comprises from 2 to 9 *****epoxide***** groups; alternatively, from 2 to 4 *****epoxide***** groups; alternatively, from 3 to 8 *****epoxide***** groups; or alternatively, from 4 to 8 *****epoxide***** groups.

DETD In some embodiments, the unsaturated ester comprises a mixture of epoxidized unsaturated esters. In this aspect, the number of *****epoxide***** groups in the epoxidized unsaturated ester is best

described as an average number of ***epoxide*** groups per epoxidized unsaturated ester molecule. In some embodiments, the epoxidized unsaturated esters have an average of at least 1.5 ***epoxide*** groups per epoxidized unsaturated ester molecule;

alternatively, an average of at least 2 ***epoxide*** groups per epoxidized unsaturated ester molecule; alternatively, an average of at least 2.5 ***epoxide*** groups per epoxidized unsaturated ester molecule; or alternatively, an average of at least 3 ***epoxide*** groups per epoxidized unsaturated ester molecule. In other embodiments, the epoxidized unsaturated esters have average of from 1.5 to 9 ***epoxide*** groups per epoxidized unsaturated ester molecule;

alternatively, an average of from 3 to 8 ***epoxide*** groups per epoxidized unsaturated ester molecule; alternatively, an average of from 2 to 4 ***epoxide*** groups per epoxidized unsaturated ester molecule; or alternatively, from of 4 to 8 ***epoxide*** group per epoxidized unsaturated ester molecule.

DETD The ***thiol*** composition can include an average of greater than 0 to about 4 ***epoxide*** groups per triglyceride. The ***thiol*** composition can also include an average of greater than 1.5 to about 9 ***epoxide*** groups per triglyceride.

DETD ***Mercaptans***

DETD Within some embodiments, an unsaturated ester or an epoxidized unsaturated ester is contacted with ***mercaptan***. Within these embodiments, the ***mercaptan*** can be any ***mercaptan*** comprising from 1 to 20 carbon atoms. Generally, the ***mercaptan*** can have the following structure: $\text{HS}-\text{R}^{\text{sup.3}}$ wherein R³ is a C1 to C20 organyl groups or a C1 to C20 hydrocarbyl groups. In further embodiments the R³ can be a C2 to C10 organyl group or a C2 to C10 hydrocarbyl group. In some embodiments, the ***mercaptan*** composition comprises a solvent. In one aspect, the ***mercaptan*** composition comprises at least one other functional group.

DETD The at least one other functional group can be selected from several different groups. For example, the at least one other functional group is an alcohol group, a carboxylic alcohol group, a carboxylic ester group, an amine group, a sulfide group, a ***thiol*** group, a methyl or ethyl ester of a carboxylic acid group, or combinations thereof. Other types of functional groups will be apparent to those of skill in the art and are to be considered within the scope of the

present invention.

DETD In some embodiments, the ***mercaptan*** is selected from the group consisting of 3-mercaptopropyl-trimethoxysilane, 2-mercaptopyridine, 4-mercaptopyridine, 2-mercaptopyrimidine, mercaptopyruvic acid, mercaptosuccinic acid, 2-mercaptonicotinic acid, 6-mercaptonicotinic acid, 2-mercaptophenol, 4-mercaptophenol, 3-mercapto-1,2-propanediol, 3-mercapto-1,2-propanediol, 3-mercapto-1-propanesulfonic acid, 1-mercapto-2-propanol, 3-mercapto-1-propanol, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzyl alcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 2-mercaptoethanesulfonic acid, 2-mercaptoethanol, 2-mercaptoethyl ether, 2-mercaptoethyl sulfide, 16-mercaptohexadecanoic acid, 6-mercapto-1-hexanol, 4'-mercaptoacetanilide, mercaptoacetic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, 2-mercaptothiazoline, 3-mercapto-1H-1,2,4-triazole, 11-mercaptoundecanoic acid, 1-mercapto-1-undecanol, or combinations thereof.

DETD In some embodiments, the ***mercaptan*** is selected from the group consisting of beta-mercaptoethanol, 2-mercaptophenol, 3-mercaptophenol, 4-mercaptophenol, 1-mercapto-2-propanol, 1-mercapto-3-propanol, mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, 2-mercaptobenzylalcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 2-mercaptoethyl ether, 2-mercaptoethyl sulfide, 6-mercapto-hexanol, 3-mercapto-1,2-propanediol, mercaptosuccinic acid, and mixtures thereof.

In further embodiments, the ***mercaptan*** is selected from the group consisting of beta-mercaptoethanol, 1-mercapto-2-propanol, 1-mercapto-3-propanol, 2-mercaptobenzylalcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 6-mercapto-hexanol, 3-mercapto-1,2-propanediol, and mixtures thereof. In further embodiments, the ***mercaptan*** is

selected from the group consisting 2-mercaptophenol, 3-mercaptophenol, 4-mercaptophenol, and mixtures thereof. In yet further embodiments, the

mercaptan is selected from the group consisting mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, mercaptosuccinic acid, and mixtures thereof.

DETD Within some embodiments, the inventive compositions described

herein

are reacted with an isocyanate compound to produce a polythiourethane composition. The isocyanate may be any isocyanates capable of reacting with the ***thiol*** esters, hydroxy ***thiol*** esters, and a cross-linked ***thiol*** esters described herein to form a polyurethane composition. Generally, the isocyanate compound has at least two isocyanate groups.

DET D In order to quantitatively measure the ***thiol*** sulfur, the ***thiol*** sulfur analyses were conducted using silver nitrate titration in accordance with ASTM D3227, with the following modifications designed to minimize probe fouling by silver salts:

the samples were diluted in a known mass of tetrahydrofuran. The silver nitrate concentration was 0.01 N standardized against potassium iodide.

DET D ***Thiol*** sulfur was analyzed by three different tests. The first

test used was the modified ASTM D3227, which resulted in a ***thiol*** sulfur measurement of 4.64%. The second test used to measure the ***thiol*** sulfur was SLP-1204, which is a test developed by Chevron

Phillips Chemical Company LLP. By using the SLP-1204 test, the resulting

thiol sulfur measurement was 4.28%. Lastly, the total sulfur was measured by combustion analysis, which resulted in a total sulfur measurement of 4.27%.

DET D Vegetable oil (42 kg) was charged to a 100-gallon holding vessel. The

vessel was purged with nitrogen and returned to atmospheric pressure.

Hydrogen sulfide (174 kg) was charged to the holding vessel. The vessel

temperature was controlled from 25-30.degree. C. while the pressure was

typically maintained between 380-400 psig. The reactants were continuously rolled from the holding tank through a stainless steel

tubular photochemical reactor containing a 7.5 KW Hanovia medium pressure mercury lamp contained within a quartz tube. Reactor temperature, pressure, and composition were monitored over the course of

the reaction. The reaction time was dependent upon reaching a desired

composition of ***thiol*** sulfur. Upon completion, the unreacted

hydrogen sulfide was slowly vented from the system. Residual H.sub.2S

was removed at 100.degree. C. and reduced pressure while passing nitrogen through a nitrogen sparge tube. The product was drained

from the bottom of the reactor into a clean drum. The ***thiol***

sulfur measurements were 11.0% when using the modified ASTM D3227, 8.74% when using SLP-1204, and the total sulfur was 11.21% when using combustion analysis (total sulfur).

DETD The resulting mercaptanized soybean oil was subjected to nitrogen sparging under reduced pressure at 100.degree. C. for a period of 4 hours to remove any residual hydrogen sulfide. The ***thiol*** sulfur measurements were 13.0% when using the modified ASTM D3227, 9.82% when using SLP-1204, and 11.69% when using combustion analysis.

DETD Table 1 provides the properties of the mercaptanized soybean oil produced in examples 1-3.

TABLE 1

Mercaptanized Soybean Oil Product Properties

Cyclic Sulfide to ***Thiol***			
Thiol Sulfur.sup..dagger. Group			
C.dbd.C to	***Thiol***	groups	
Example	(wt %)	Molar Ratio	Molar Ratio
1	4.28	0.02	2.79
2	11.0	0.03	0.26
3	13.0	0.03	0.51

.sup..dagger. ***Thiol*** sulfur content determined by the modified ASTM D3227

DETD Soybean oil was charged to a 1000 gallon stirred reactor. Hydrogen sulfide was then charged to the reactor. After the hydrogen sulfide was charged to the reactor, the stirrers and the UV lamps were turned on and the reaction allowed to build temperature and pressure as the reaction proceed. The reaction was continued until a minimum ***thiol*** sulfur content of 8 weight percent was achieved. After reaction was completion, the excess hydrogen sulfide was flashed from the reactor.

For runs 2-5, the mercaptanized soybean oil product underwent an additional hydrogen sulfide stripping step comprising stripping hydrogen sulfide from the product under vacuum, 50 mm Hg, at 250.degree. F. (only true for runs 2-5).

DETD Table 3 provides the details of the analysis of the mercaptanized soybean oil producing in the five 1000 gallon reactor runs.

TABLE 3

1000 gallon reactor Mercaptanized Soybean Oil Product Properties

Side Chain

Thiol Cyclic Sulfide to ***Thiol*** C.dbd.C				
to				
Run	***Thiol***	Containing		
	Sulfur.sup..dagger.	Group	groups	
Number	***Thiol***	Groups		
	(wt %)	Molar Ratio	Molar Ratio	(%)
1	9.3	--	--	71.6
2	9.6	0.04	0.48	72.3
3	9.2	0.03	0.59	69.1
4	9.3	0.03	0.62	71.6
5	10.1	0.03	0.54	72.3

.sup..dagger. ***Thiol*** sulfur content determined by Raman spectroscopy

Mercaptanized Castor Bean Oil
 DETD The analytical properties of the two mercaptanized castor oil products

are provide in Table 4.

TABLE 4

Mercaptanized Castor Oil Product Properties

Thiol C.dbd.C to Side Chain			
Containing	Sulfur.sup..dagger. ***Thiol*** groups		
Thiol			
Groups			
Example	(wt %)	Molar Ratio	(%)
1	6.4	0.52	64.1
2	7.4	0.26	77.7

.sup..dagger. ***Thiol*** sulfur content determined by Raman spectroscopy

Mercaptohydroxy Soybean Oil Synthetic Procedure
 DETD Epoxidized Soybean Oil (700 g, .about.0.7 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 4.7 g, 30.5 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 132.0 g, 3.87 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 8 hrs, during which time the reactor pressure decreased from a maximum of 351 psig to 219 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content

of 7.53

wt. %, 2.5 SH/molecule, or 2.35 meq SH/g. Combustion analysis indicated

C, 64.37%, H, 10.20%, N, <0.15%, and S, 9.51%.

DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure

tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was

then pressured into the stirred reactor contents through a dip tube in

the liquid space. The reaction mixture was heated and maintained at

97.degree. C. with stirring for 14 hrs, during which time the reactor

pressure decreased from a maximum of 509 psig to 229 psig. The stirrer

was stopped and while still warm (90-95.degree. C.), excess H.sub.2S was

slowly vented to a low-pressure flare. The reactor vapor space was then

swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged

under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a

thiol sulfur (titration by modified ASTM D3227) content

of 4.14

wt. %, 1.4 SH/molecule, or 1.29 meq SH/g. Combustion analysis indicated

C, 65.18%, H, 10.17%, N, <0.15%, and S, 7.80%.

DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure

tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was

then pressured into the stirred reactor contents through a dip tube in

the liquid space. The reaction mixture was heated and maintained at

85.degree. C. with stirring for 10 hrs, during which time the reactor

pressure decreased from a maximum of 578 psig to 489 psig. The stirrer

was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was

slowly vented to a low-pressure flare. The reactor vapor space was then

swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged

under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a

thiol sulfur (titration with modified ASTM D3227)

content of
8.28 wt. %, 2.8 SH/molecule, or 2.58 meq SH/g. Combustion
analysis indicated C, 65.24%, H, 9.52%, N, 0.18%, and S, 9.53%.
DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were
charged to a 1-L Hastelloy C autoclave reactor that was pressure tested
to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then
pressured into the stirred reactor contents through a dip tube in the
liquid space. The reaction mixture was heated and maintained at
85.degree. C. with stirring for 12 hrs, during which time the reactor pressure
decreased from a maximum of 587 psig to 498 psig. The stirrer was
stopped and while still warm (80-85.degree. C.), excess H.sub.2S
was slowly vented to a low-pressure flare. The reactor vapor space
was then swept with N.sub.2 for 1 hr and the reactor contents drained warm
(80-85.degree. C.). The reaction product was N.sub.2 sparged
under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove
residual H.sub.2S. The resulting light yellow, viscous sticky oil had a
thiol sulfur (titration by modified ASTM D3227) content
of 8.24 wt. %, 2.8 SH/molecule, or 2.57 meq SH/g. Combustion analysis
indicated C, 63.39%, H, 10.01%, N, <0.15%, and S, 8.76%.
DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were
charged to a 1-L Hastelloy C autoclave reactor, and the vessel was
pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99
mol) was then pressured into the stirred reactor contents through a dip
tube in the liquid space. The reaction mixture was heated and maintained
at 85.degree. C. with stirring for 8 hrs, during which time the
reactor pressure decreased from a maximum of 606 psig to 537 psig. The
stirrer was stopped and while still warm (80-85.degree. C.), excess
H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space
was then swept with N.sub.2 for 1 hr and the reactor contents drained warm
(80-85.degree. C.). The reaction product was N.sub.2 sparged
under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove
residual H.sub.2S. The resulting light yellow, viscous sticky oil had a
thiol sulfur (titration by modified ASTM D3227) content
of 7.34 wt. %, 2.5 SH/molecule, or 2.29 meq SH/g. Combustion analysis

indicated

C, 64.47%, H, 10.18%, N, <0.15%, and S, 8.40%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630

psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured

into the stirred reactor contents through a dip tube in the liquid

space. The reaction mixture was heated and maintained at 85.degree. C.

with stirring for 6 hrs, during which time the reactor pressure decreased from a maximum of 586 psig to 556 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S

was

slowly vented to a low-pressure flare. The reactor vapor space

was then

swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged

under

vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove

residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content

of 5.93

wt. %, 2.0 SH/molecule, or 1.85 meq SH/g. Combustion analysis

indicated

C, 65.26%, H, 10.19%, N, <0.15%, and S, 8.43%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure

tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was

then pressured into the stirred reactor contents through a dip tube in

the liquid space. The reaction mixture was heated and maintained at

85.degree. C. with stirring for 4 hrs, during which time the reactor

pressure decreased from a maximum of 595 psig to 554 psig. The stirrer

was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was

slowly vented to a low-pressure flare. The reactor vapor space was then

swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged

under

vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove

residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a ***thiol*** sulfur (titration by modified ASTM D3227) content

of 5.36

wt. %, 1.8 SH/molecule, or 1.67 meq SH/g. Combustion analysis

indicated

C, 65.67%, H, 10.17%, N, 0.34%, and S, 9.84%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and
 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were
charged
 to a 1-L Hastelloy C autoclave reactor that was pressure tested
to 630
 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then
pressured
 into the stirred reactor contents through a dip tube in the
liquid
 space. The reaction mixture was heated and maintained at
85.degree. C.
 with stirring for 4 hrs, during which time the reactor pressure
decreased from a maximum of 577 psig to 519 psig. The stirrer was
stopped and while still warm (80-85.degree. C.), excess H.sub.2S
was
 slowly vented to a low-pressure flare. The reactor vapor space
was then
 swept with N.sub.2 for 1 hr and the reactor contents drained warm
(80-85.degree. C.). The reaction product was N.sub.2 sparged
under
 vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove
residual
 H.sub.2S. The resulting light yellow, viscous sticky oil had a
 thiol sulfur (titration with AgNO.sub.3) content of
5.85 wt. %,
 2.0 SH/molecule, or 1.82 meq SH/g. Combustion analysis indicated
C,
 65.09%, H, 10.15%, N, 0.35%, and S, 10.63%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and
 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were
charged
 to a 1-L Hastelloy C autoclave reactor, and the vessel was
pressure
 tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99
mol) was
 then pressured into the stirred reactor contents through a dip
tube in
 the liquid space. The reaction mixture was heated and maintained
at
 85.degree. C. with stirring for 2 hrs, during which time the
reactor
 pressure decreased from a maximum of 577 psig to 508 psig. The
stirrer
 was stopped and while still warm (80-85.degree. C.), excess
H.sub.2S was
 slowly vented to a low-pressure flare. The reactor vapor space
was then
 swept with N.sub.2 for 1 hr and the reactor contents drained warm
(80-85.degree. C.). The reaction product was N.sub.2 sparged
under
 vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove
residual
 H.sub.2S. The resulting light yellow, viscous sticky oil had a
 thiol sulfur (titration by modified ASTM D3227) content
of 5.07
 wt. %, 1.7 SH/molecule, or 1.58 meq SH/g. Combustion analysis
indicated
 C, 63.96%, H, 10.01%, N, 0.35%, and S, 11.22%.

DETD Table 5 provides the properties of the mercaptohydroxy soybean
oil

samples produced in Examples 1-10.

TABLE 5

Example	***Epoxides***		***Mercaptan***		
	Reaction	Reaction	Sulfur	SH per	groups left
	Time (hrs)	Temp (.degree. C.)	(wt. %).1	molecule.2	
per	***Epoxide***	:SH			
	molecule. ³	Molar Ratio			
1	0	N/A	N/A	0	4.3
2	8	85	7.53	2.5	1.8
3	14	97	4.14	1.4	2.9
4	10	85	8.28	2.8	1.5
5	12	85	8.24	2.8	1.5
6	8	85	7.34	2.5	1.8
7	6	85	5.93	2.0	2.3
8	4	85	5.36	1.8	2.5
9	4	85	5.85	2.0	2.3
10	2	85	5.07	1.7	2.6

¹Thiol sulfur was determined by silver nitrate oxidation using ASTM D 3227

²Determined by wt. % ***thiol*** sulfur

³Determined by subtracting the SH/molecule from the starting material

epoxide content

DETD Epoxidized soybean oil and the catalyst were charged to a 1-L Hastelloy

C autoclave reactor, and the vessel was pressure tested to 1000 psig.

Hydrogen sulfide was then pressured into the stirred reactor contents

through a dip tube in the liquid space. The reaction mixture was heated

and maintained at temperature a set period of time with stirring for 12

hrs. During the reaction time the reactor pressure usually decreased. At

the end of the reaction time, the stirrer was stopped and excess H₂S was slowly vented while the reaction mixture was warm to

a low-pressure flare. The reactor vapor space was then swept with

N₂ for 1 hr and the reactor contents drained. The reaction product

was

N₂ sparged under vacuum (<50 mmHg) at 100.degree. C. for 16

hrs to
 remove residual H.sub.2S. Table 6 provides the reaction
 conditions used
 to produce the mercaptohydroxy soybean oils for several runs and
 the
 thiol sulfur content of the mercaptohydroxy soybean
 oils
 produced.

TABLE 6

Mercaptohydroxy Soybean Oil Production Runs

Run (minutes)	Epoxidized Soybean Oil		Catalyst (g)	H.sub.2S ***Thiol*** (g)	H.sub.2S: Sulfur.sup.a Molar Ratio	***Epoxide*** Sulfur.sup.a (.degree. C.)
	Temperature	Time				
	(g)	(g)				
	(wt. %)					
556-41.sup..dagger.	249.6			1.950	214.0	5.86
728	5.69					64
556-53.sup..dagger.	250.0			2.000	213.0	5.81
370	9.04					100
556-47.sup..dagger.	250.5			1.050	213.0	5.81
720	10.47					101
407-81D.sup..dagger.	500.0			4.200	255.0	3.49
480	7.53					85
407-86.sup..dagger.	600.0			5.000	204.0	2.07
600	8.28					85
556-79.sup..dagger-dbl.	250.0			2.600	214.0	5.83
720	6.68					100
556-80.sup..dagger-dbl.	251.0			5.000	214.0	5.81
720	9.51					100

.sup..dagger.Catalyst was DBU
 .sup..dagger-dbl.catalyst was triethylamine (TEA)
 .sup.aThiol sulfur measured by silver nitrate titration using modified
 ASTM D

3227

DETD Run number 407-86 was subjected to the sodium methoxide
 methanolysis

procedure and subsequently analyzed by GC/MS. The GS/MS analysis
 indicated that the product had ***epoxide*** group to

thiol
 group molar ratio of approximately 0.14. The methanolysis data
 also

indicated that an average of 80.4 percent of the product
 mercaptohydroxy
 soybean oil contained sulfur.

DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % ***thiol***
 sulfur,) was charged to a three necked flask along with elemental
 sulfur

pellets (9.6 g). The reaction mixture was heated to 120.degree.
 C. until

sulfur dissolved and then cooled to 99.degree. C. Tributylamine
 (4.8 g)

was charged to the reaction mixture with an addition funnel drop
 wise.

The reaction mixture was mixed at 90.degree. C. for 2 hrs.
 H.sub.2S

evolution was observed. The reaction product (904.8 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a ***thiol*** sulfur of 6.33 wt. % (by modified ASTM D3227). The elemental combustion analysis was 70.19% C, 10.37% H; and 11.21% S.

DETD Mercaptanized soybean oil (900.0 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur pellets (36.0 g). The reaction mixture was heated to 120.degree. C. until sulfur dissolved and then cooled to 100.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 36 hrs. H.sub.2S evolution was observed. The reaction product (825.6 g) was sparged with N.sub.2 under vacuum at 90.degree. C. for 36 hrs to remove residual H.sub.2S. The reaction product was then sparged with N.sub.2 under vacuum at 110.degree. C. for 3 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a ***thiol*** sulfur of 2.36 wt. % (by modified ASTM D3227). The elemental combustion analysis was 68.90% C; 11.07% H; and 12.25% S.

DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur pellets (18.0 g). The reaction mixture was heated to 125.degree. C. until sulfur dissolved and then cooled to 101.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H.sub.2S evolution was observed. The reaction product (901.5 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a ***thiol*** sulfur of 4.9 wt. % (by modified ASTM D3227). The elemental combustion analysis was 69.58% C, 11.25% H; and 11.31% S.

DETD Mercaptanized soybean oil (900.2 g; 10.92 wt. % ***thiol*** sulfur,) was charged to a three necked flask along with elemental sulfur pellets (45.0 g). The reaction mixture was heated to 125.degree. C. until sulfur dissolved and then cooled to 100.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs.

H.sub.2S evolution was observed. The reaction product (915.0 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a sulfur of 1.41 wt. % (by modified ASTM D3227). The elemental combustion analysis was 68.35% C, 10.98% H; and 13.28% S.

DETD Numerous polythiourethane compositions were prepared by reacting a ester composition with a diisocyanate in the presence of a catalyst by using the processes described herein for preparing such polythiourethane compositions. The compositions were produced using the different variables of feedstocks, diisocyanates, stoichiometry, and catalysts shown in Table 8. Once every combination of variable was used, over 1200 compositions were produced. Each of the feedstocks were reacted with each of the diisocyanates at each of the stoichiometries with each of the catalysts listed to produce the 1200+ compositions. The stoichiometry was based upon a ester composition (MSO, MHSO, CMSO, MCO) active hydrogen (and hydroxyl group) to diisocyanate equivalent ratio. For example, castor oil was reacted with toluene diisocyanate at a stoichiometric value of 1.25 while using Jeffol.RTM. A-480 as the catalyst. As another example, a ester composition was reacted with methane diisocyanate at a stoichiometric value of 0.9 while using the DABCO catalyst.

DETD In the first MCO polythiourethane example, MCO was weighed into a polyethylene beaker. To the MCO agent was added Luprinate at a to isocyanate mole ratio of 0.95. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick. The entire pre-polymer mixture was then poured into a mold for curing and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer.

DETD In the second MCO polythiourethane example, MCO was weighed into a polyethylene beaker. To the MCO agent was added Luprinate M20S at a

thiol to isocyanate mole ratio of 1.00. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick. The entire pre-polymer mixture was then poured into a mold for curing and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer.

DETD In the polythiourethane compositions, the feedstock ***thiol*** ester compositions that were used included MSO (mercaptanized soybean oil), MHSO (mercaptohydroxy soybean oil), CMSO (cross-linked mercaptanized soybean oil), castor oil, and MCO (mercaptanized castor oil). The diisocyanates that were used to produce these compositions included MDI (4,4'-methylenebis(phenyl) diisocyanate), HMDI (4,4'-methylenebis(cyclohexyl) diisocyanate, which is also known as hydrogenated MDI), TDI (tolylene 2,4-diisocyanate), HDI (1,6-diisocyanatohexane, which is also known as hexamethylene diisocyanate), and Luprinat.TM. M20S (which is an oligomerized form of MDI and is also referred to as polymeric MDI that is produced by BASF Corporation). The catalysts that were used included DABCO (diazabicyclooctane--di-tertiary amine), DBTDL (dibutyl tin dilaurate--organometallic catalyst), Jeffol.RTM. A-480 (which is a tertiary amine polyol produced by Huntsman Based Chemicals), and BDMA (benzyldimethylamine).

DETD In the Fertilizer Examples, the following materials were used:

A: Fertilizer particles--granular fertilizer grade urea, SGN 250, commercially available from Agrium;

B1: Mercaptanized soybean oil (an example of MVO discussed above)--Polymercaptan 358, available from Chevron Phillips Chemical Co.; 8.65% ***thiol*** sulfur; 370 equivalent weight; viscosity of 510.6

cSt @ 21.degree. C.;

B2: Mercapto-hydroxy soybean oil (an examples of MHVO discussed above)--A

mercapto-hydroxy soybean oil made by the free radical addition of hydrogen sulfide to epoxidized soybean oil; the mercapto and hydroxy

functionalities are equal; 8.335% ***thiol*** sulfur; equivalent

weight 192 (including both mercapto and hydroxy functionalities);

B3: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil

made by the addition of elemental sulfur to mercaptanized soybean oil;
 thiol sulfur content 6.33%; equivalent weight 506;
 B4: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO
 discussed above)--A sulfur cross-linked mercaptanized soybean oil
 made by the addition of elemental sulfur to mercaptanized soybean oil;
 thiol sulfur content 7.64%; equivalent weight 419;
 cross-linkcross-link
 C1: Isocyanate #17--A polymeric MDI, commercially available from BASF
 Canada,
 equivalent weight of 133;
 C2: Epoxy resin--5 minute epoxy resin, commercially available from ITW
 Devcon,
 Danvers, Mass. 01923 USA, equivalent weight 198;
 D1: Organic additive--Gulftene C30-HA alpha olefin wax, commercially
 available
 from Chevron Phillips Chemical Co., melting point 65.degree.
 C.-80.degree. C.;
 D2: Organic additive--Calwax 170, a microcrystalline wax commercially
 available from Calwax Corporation;
 E: Cross-linking agent--Jeffol A480, commercially available from
 Huntsman
 Polyurethanes; equivalent weight of 120; functionality 4.0;
 viscosity of
 4000 cPs @25C;
 F1: Amine catalyst: Exp-9, commercially available from Huntsman
 Polyurethanes;
 and
 F2: Amine catalyst: 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU), CAS#
 6674-22-2 .
 DETD Analysis of the ***Thiol*** Containing Esters, Hydroxy
 Thiol Containing Esters and Cross-Linked ***Thiol***
 Containing Ester
 DETD Particular aspects of the ***thiol*** containing esters,
 hydroxy
 thiol containing esters, cross-linked ***thiol***
 ester,
 unsaturated esters and epoxidized unsaturated esters are measured
 particular analytical techniques. ***Thiol*** sulfur values
 were
 obtained using a silver nitrate titration as described in ASTM
 D3227 or
 by Raman spectroscopy. Carbon-carbon double bond to ***thiol***
 group molar ratio, cyclic sulfide to ***thiol*** group molar
 ratios
 were determined by .sup.13C NMR and/or GC analysis of the
 thiol
 containing ester or hydroxy ***thiol*** containing ester side
 chains.
 DETD ***Thiol*** Sulfur Content by Raman Spectroscopy
 DETD ***Thiol*** sulfur content was measured by both silver
 nitrate
 titration, ASTM D3227, and/or Raman spectroscopy. The Raman
 spectroscopy
 method is practiced by measuring the Raman spectra of the
 thiol
 containing ester, hydroxy ***thiol*** containing ester,
 cross-linked
 thiol ester and comparing the spectra to calibration

standards
containing known ***thiol*** compounds having known amounts of
thiol groups. Generally, the calibration standard
thiol
compound has a similar structure to the ***thiol***
containing
esters analyzed.
DETD The ***thiol*** containing esters, hydroxy ***thiol***
containing esters and cross-linked ***thiol*** ester
thiol
content were determined by comparing the Raman spectra of the
thiol containing esters, hydroxy ***thiol***
containing
esters and cross-linked ***thiol*** ester to calibration
standards
prepared from mercaptanized methyl oleate diluted in soybean oil
to
known ***thiol*** sulfur contents. ***Thiol*** sulfur
calibration standards were prepared using standards using various
known
concentration of mercaptanized methyl oleate diluted in soybean
oil.
DETD Raman spectra of the calibration standards and the ***thiol***
containing esters, hydroxy ***thiol*** containing esters and
cross-linked ***thiol*** ester were measured using a Kaiser
Hololab
5000 Process Raman spectrometer, using a 785 nm laser.
Thiol
containing esters, hydroxy ***thiol*** containing esters and
cross-linked ***thiol*** ester samples and the ***thiol***
sulfur calibration standard Raman spectra were obtained by
collecting
four 10 second scans which were then processed using Holoreact
software.
Thiol sulfur values for the ***thiol*** containing
esters,
hydroxy ***thiol*** containing esters and cross-linked
thiol
ester were then calculated using the ratio of the peak area
values of
the ***thiol*** SH peak (center: 2575 cm⁻¹; area 2500-2650
cm⁻¹),
and the C.dbd.O peak (center--1745 cm⁻¹; area--1700-1800 cm⁻¹)
and
comparing them to the peak area values for the calibration
standards and
interpolating the containing esters, hydroxy ***thiol***
containing
esters and cross-linked ***thiol*** ester ***thiol***
sulfur
contents. Repeatability of the ***thiol*** sulfur values as
measured
by Raman spectroscopy have been shown to have a standard
deviation of
0.05-0.1 and a % RSD of 0.6-1.5 using 5 samples having a %
thiol
sulfur content ranging from 3.1-10.6 weight percent as measured
over a
two month period.
DETD The Raman spectroscopy technique for determining the

thiol
 sulfur content of a ***thiol*** containing ester, hydroxy
 thiol containing ester, and a cross-linked
 thiol
 containing ester has been illustrated using a ***thiol***
 containing
 ester produced from soybean oil. However, one skilled in the art
 may
 adapt and apply the Raman spectroscopy technique for determining
 the
 thiol sulfur content of other ***thiol***
 containing esters,
 hydroxy ***thiol*** containing esters, and a cross-linked
 thiol containing esters described herein.
 DETD C.dbd.C to ***Thiol*** Group and Cyclic Sulfide Group to
 Tool Group
 Molar Ratios by .sup.13C NMR
 DETD Carbon-carbon double bond to ***thiol*** group molar ratio
 and
 cyclic sulfide group to ***thiol*** group molar ratios were
 determined by .sup.13C NMR. ***Thiol*** containing ester
 .sup.13C
 NMR spectra were obtained on a Varian Mercury INOVA400 NMR, a
 Varian
 Mercury Plus 300 NMR, or equivalent spectrometer (75.5 MHz
 .sup.13C
 NMR). Peak areas were determined for the cyclic sulfide carbon
 atoms,
 thiol group HS--C carbon atoms and carbon-carbon double
 bonds
 carbon atoms using the .sup.13C NMR regions indicated in the
 table
 below:

Functional Group	.sup.13C NMR Region	Number of Carbon Atoms/Group
Cyclic Sulfide Carbon Atoms	49-49.5 ppm	2
HS--C Carbon Atoms	40-41.5 ppm	1
C.dbd.C Carbon Atoms	120-140 ppm	2
DETD The ***thiol*** containing ester cyclic sulfide to ***thiol*** group molar ratio were calculated by dividing the cyclic sulfide carbon atoms .sup.13C NMR peak area by 2 (to account for the 2 carbon atoms per cyclic sulfide group) and dividing the resultant number by the ***thiol*** group HS--C carbon atoms .sup.13C NMR peak area. The ***thiol*** containing ester carbon-carbon double bond to ***thiol*** group molar ratio were calculated by dividing the C.dbd.C carbon atoms .sup.13C NMR peak area by 2 (to account for the 2 carbon atoms per carbon-carbon double bond) and dividing the result number by the ***thiol*** group HS--C carbon atoms .sup.13C NMR peak area Offset sample .sup.13C NMR's for soybean oil and a ***thiol***		

containing ester produced from soybean oil using the disclosed process is provided as FIG. 1.

DETD The NMR technique for analyzing the unsaturated ester and the ***thiol*** containing ester produced from an unsaturated ester have been illustrated using ¹³C NMR on soybean oil the ***thiol*** containing ester produced from soybean oil. However, one skilled in the art may adapt and apply either the ¹³C NMR or ¹H NMR technique to analyze the unsaturated esters and ***thiol*** containing ester produced from the unsaturated ester described herein.

DETD ***Epoxide*** Group to ***Thiol*** Group Molar Ratios by ¹³C or ¹H NMR

DETD The ***epoxide*** group to ***thiol*** group molar ratios were determined using ¹H or ¹³C NMR. Hydroxy ***thiol*** containing ester ¹H or ¹³C NMR spectra were obtained on a Varian Mercury INOVA400 NMR, a Varian Mercury Plus 300 NMR, or equivalent spectrometer (300 MHz ¹H NMR-75.5 MHz ¹³C NMR).

Peak areas were determined for the ***epoxide*** group and sulfide group using the ¹³C and or ¹H regions indicated in the table below:

Functional Group	¹ H NMR Region	¹³ C NMR Region	Number of Carbon Atoms/Group	Number of Hydrogen Atoms/Group
Epoxide Group	2.75-3.2 ppm	53.6-56.6 ppm	2	2
Carbon Atoms				
HS--C Carbon Atoms	3.2-4 ppm	40-41.5 ppm	1	1
DETD The hydroxy ***thiol*** containing ester ***epoxide*** group to ***thiol*** group molar ratio were calculated by dividing the ***epoxide*** group carbon atoms ¹ H NMR peak area by 2 (to account for the 2 hydrogen atoms attached to the ***epoxide*** carbon atoms) and dividing the result number by the ***thiol*** group HS--C carbon atom hydrogens ¹³ C NMR peak area. Similarly, the hydroxy ***thiol*** containing ester ***epoxide*** group to ***thiol*** group molar ratio were calculated using ¹³ H NMR peak areas.				
DETD The average number of ***epoxide*** group per epoxidized unsaturated ester molecule can be determined utilizing similar methods				

utilizing either the carbonyl group carbon atom or the C--O ester group carbon atoms .sup.13C NMR peak areas in conjunction with the ***epoxide*** group .sup.13C NMR peak area. Sample .sup.1H NMR's epoxidized soybean oil and a ***thiol*** containing ester produced from epoxidized soybean oil 1 are provided in FIG. 2.

DETD The NMR technique for analyzing the epoxidized unsaturated ester and the ***thiol*** containing ester produced from an epoxidized unsaturated ester (a hydroxy ***thiol*** containing ester) has been illustrated using .sup.1H NMR on epoxidized soybean oil the ***thiol*** containing ester produced from epoxidized soybean oil.

However, one skilled in the art may adapt and apply either the .sup.1H NMR or .sup.13C NMR technique to analyze the epoxidized unsaturated esters and ***thiol*** containing ester produced from the epoxidized unsaturated ester described herein.

DETD Analysis of Unsaturated Esters, Epoxidized Unsaturated Esters, ***Thiol*** Containing Esters, and Hydroxy ***Thiol*** Containing Esters by Methanolysis

DETD Many properties of the unsaturated esters, epoxidized unsaturated esters, ***thiol*** containing esters, and hydroxy ***thiol*** containing ester were and/or can be determined by converting the complex ester molecules into their component polyols and carboxylic acid methyl esters. The converted esters are then analyzed by gas chromatography (GC) and/or gas chromatography/mass spectrometry (GCMS) to determine the composition of the complex ester side chains. Properties that are or can be determined by the methanolysis followed by GC or GC/MS of the carboxylic acid methyl esters include the number of side chain that contain ***thiol*** groups, the percent of ***thiol*** group sulfur, the number of (or average number) of double bonds per ester molecule, the molecular weight distribution (or average molecular weight) of the ester side chains, The number of (or average number of) ***epoxide*** groups per ester molecule, the cyclic sulfide to ***thiol*** group molar ratio, the carbon-carbon double bond to ***thiol*** group molar ratio, and the ***epoxide*** group to ***thiol*** group molar ratio, among others.

DETD Depending upon the material being subjected to the methanolysis procedure, there are two methanolysis procedures that were

practiced

upon the unsaturated ester, epoxidized esters, ***thiol***
containing ester, and hydroxy ***thiol*** containing esters
described within the experimental section.

DETD Unsaturated esters and ***thiol*** containing ester produced
from

unsaturated ester were subjected to a hydrogen chloride based
methanolysis procedure. In the hydrogen chloride methanolysis
procedure,
a 50 to 100 mg sample of the ***thiol*** containing ester is
contacted with 3 mL of 3 N methanolic HCl and reacted for 2 hours
a

50.degree. C. The solution is then allowed to cool and the
neutralized
with a dilute sodium bicarbonate solution. The solution's organic
components are then extracted with ethyl ether and analyzed by GC
and/or

GC/MS. Additional details for the methanolic hydrogen chloride
methanolysis procedure may be found in the product specification
sheet

for methanolic HCl, 0.5 N and 3 N as supplied by Supelco.

DETD Epoxidized unsaturated esters and hydroxy ***thiol***
containing
esters produced from epoxidized unsaturated esters were subjected
to a

sodium methoxide based methanolysis procedure. The sodium
methoxide
methanolysis procedure was based upon the procedure disclosed in
U.S.

Pat. No. 3,991,089. In the sodium methoxide methanolysis
procedure,
approximately 1 g of the ester was placed in a 50 mL vial with
5.0 mL

25% sodium methoxide in methanol, and 10 mL methanol. The mixture
was
shaken for approximately 1 hour at room temperature, during which
time

the solution became one phase. The mixture was then poured into
25 mL of
distilled water. Diethyl ether, 25 mL, was added to the solution
and the

mixture was acidified with 0.5 N HCL to a pH of approximately 5.
The

organic layer was separated from the aqueous layer using a
separatory
funnel. The organic layer was washed successively with distilled
water

(15 mL) and brine solution (15 mL) and then dried over magnesium
sulfate. The magnesium sulfate was separated from the organic
solution

by filtration and the solvent removed by rotary evaporation.

DETD FIG. 3 provides a GC/MS trace of a mercaptanized soybean oil
subjected
to the methanolysis procedure and analyzed by GC/MS using a HP-5
30

m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column.

Table 11
provides the GC/MS trace peak assignments.

TABLE 11

GC/MS Data for Methanolysis of A ***Thiol*** Containing Ester
 Produced from
 Soybean Oil

GC Retention time	Methyl Ester Carboxylic Acid Assignment
21.58	Methyl hexadecanoate
23.66	Methyl (C18 monoene)oate
23.74	Methyl (C18 monoene)oate
23.96	Methyl octadecanoate
26.46	Methyl (C18 Monoene monomercaptan)oate
26.59	Methyl (C18 Monoene monomercaptan)oate
26.66	Methyl (C18 Monoene monomercaptan)oate
26.80	Methyl (C18 monomercaptan)oate
27.31	Methyl (C18 cyclic sulfide)oate
27.44	Methyl (C18 cyclic sulfide)oate
29.04	Methyl (C18 dimercaptan)oate
29.15	Methyl (C18 dimercaptan)oate
29.37	Methyl (C18 monoene dimercaptan)oate
29.46	Methyl (C18 monoene dimercaptan)oate
30.50	Methyl (C18 di (cyclic sulfide))oate

Peaks at 29.37 or 29.46 could also contain Methyl (C18 cyclic sulfide monomercaptan)oate isomers as part of those peaks.

DETD FIG. 5 provides a GC/MS trace of an epoxidized soybean oil contacted

with hydrogen sulfide (a hydroxy ***thiol*** containing ester)

subjected to the methanolysis procedure and analyzed by GC/MS using a

HP-5 30 m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column.

Table 13 provides the GC/MS trace peak assignments.

TABLE 13

GC/MS Data for Methanolysis of a Hydroxy ***Thiol*** Containing Ester
 Produced from Epoxidized Soybean Oil

GC Retention time	Methyl Ester Carboxylic Acid Assignment
-------------------	---

16.09	Methyl hexadecanoate
17.68	Methyl octadecanoate
18.94	Methyl (C18 monoepoxide)oate
19.94	Methyl (C18 diepoxide)oate
20.14	Methyl (C18 diepoxide)oate
20.75	Methyl (C18 monohydroxy monothiol)oate
21-21.5	Methyl (C18 triepoxide)oate
22.82	Methyl (C18 dihydroxy dithiol)oate
22.90	Methyl (C18 monoepoxide monohydroxy monothiol)oate
27-27.5	Unidentified mixture of C18 sulfur containing methyl esters

DETD The methanolysis procedure and GC/MS procedure has been illustrate

using soybean oil, epoxidized soybean oil, and the ***thiol*** containing products derived from soybean oil and epoxidized soybean oil.

However, one skilled in the art can easily adapt the procedures

to the analysis of other unsaturated esters, epoxidized unsaturated ester, and the ***thiol*** containing products derived from the unsaturated esters and epoxidized unsaturated esters as described herein.

DETD The polythiourethane produced from the ***thiol*** containing esters, hydroxy ***thiol*** containing esters, and cross linked ***thiol*** containing ester were analyzed using ASTM E1545-95A and E228-95 to provide the glass transition temperatures and the coefficients of thermal expansion. Shore hardness of the polythiourethanes were determined using ASTM D2240-02A. The polythiourethane were also subject to a subjective analysis classifying the polythiourethanes as hard, flexible, rubbery, rigid, tough, brittle, and other characteristics.

CLM What is claimed is:

1. A cross-linked ***thiol*** ester composition comprising ***thiol*** ester oligomers having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1.

CLM What is claimed is:

2. The cross-linked ***thiol*** ester composition of claim 1, wherein the ***thiol*** ester oligomers have at least three ***thiol*** ester monomers connected by polysulfide linkages.

CLM What is claimed is:

3. The cross-linked ***thiol*** ester composition of claim 1, wherein the ***thiol*** ester oligomers have from 3 to 20 ***thiol*** ester monomers connected by polysulfide linkages.

CLM What is claimed is:

4. The cross-linked ***thiol*** ester composition of claim 1, wherein the crosslinked ***thiol*** ester composition comprises ***thiol*** ester monomers and ***thiol*** ester oligomers.

CLM What is claimed is:

5. The cross-linked ***thiol*** ester composition of claim 4, wherein the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total ***thiol*** sulfur content from 0.5 to 8 weight percent.

CLM What is claimed is:

6. The cross-linked ***thiol*** ester composition of claim 4, wherein the combined ***thiol*** ester monomers and ***thiol*** ester oligomers have an average molecular weight greater than 2000.

CLM What is claimed is:

7. The cross-linked ***thiol*** ester composition of claim 4, wherein the ***thiol*** ester monomers and ***thiol*** ester oligomers have an average molecular weight from 2000 to 20,000.

CLM What is claimed is:
8. The cross-linked ***thiol*** ester composition of claim 4, wherein the ***thiol*** ester monomers and ***thiol*** ester oligomers have a total sulfur content ranging from 8 to 15 weight percent.

CLM What is claimed is:
9. A cross-linked ***thiol*** ester composition produced by the process comprising the steps of: a) contacting a ***thiol*** ester composition with an oxidizing agent; and b) reacting the ***thiol*** ester and the oxidizing agent to form ***thiol*** ester oligomers having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1.

CLM What is claimed is:
10. A process to produce a cross-linked ***thiol*** ester composition comprising: a) contacting a ***thiol*** ester composition with an oxidizing agent; and b) reacting the ***thiol*** ester and the oxidizing agent to form ***thiol*** ester oligomers having at least two ***thiol*** ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1.

CLM What is claimed is:
13. The process of claim 10, wherein the ***thiol*** ester is a hydroxy ***thiol*** ester.

CLM What is claimed is:
14. The process of claim 10, wherein a weight ratio of elemental sulfur to ***thiol*** sulfur in the ***thiol*** ester molecules ranges from 0.5 to 32.

CLM What is claimed is:
15. The process of claim 10, wherein step of the reacting the ***thiol*** ester and the oxidizing agent is performed at a temperature ranging from 25.degree. C. to 150.degree. C.

CLM What is claimed is:
16. The process of claim 10, wherein residual hydrogen sulfide is stripped from the cross-linked ***thiol*** ester composition produced.

CLM What is claimed is:

17. The process of claim 12, wherein the reaction of the
thiol
ester and the elemental sulfur is catalyzed.

IT 102-85-2, Tri-n-butylphosphite ***6674-22-2*** ,
1,8-Diazabicyclo[5.4.0]undec-7-ene
(activator; thiol ester compns. prepd. by reacting H₂S with
unsatd.
esters, such as soybean oil for manuf. monomers for prodn. of
polythiourethanes for fertilizers)

L7 ANSWER 49 OF 60 USPATFULL on STN

ACCESSION NUMBER: 1999:128662 USPATFULL <<LOGINID::20091205>>

TITLE: Reacting methylene and alkene components in
presence of

INVENTOR(S): tertiary amine reacted with ***epoxide***
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	NUMBER	KIND	DATE
PATENT INFORMATION:	US 5969046		19991019
APPLICATION INFO.:	US 1991-683126		19910409 (7)
RELATED APPLN. INFO.:	Continuation of Ser. No. US 1989-338433, filed on 13 Apr 1989, now abandoned which is a continuation of Ser. No. US 1986-952122, filed on 18 Nov 1986, now abandoned		
DOCUMENT TYPE:	Utility		
FILE SEGMENT:	Granted		
PRIMARY EXAMINER:	Sellers, Robert E.		
LEGAL REPRESENTATIVE:	Bakule, Patent Agent, Ronald D.		
NUMBER OF CLAIMS:	33		
EXEMPLARY CLAIM:	1		
LINE COUNT:	2014		

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI Reacting methylene and alkene components in presence of tertiary
amine

reacted with ***epoxide***

AB A method for reacting a methylene-containing component such as an
acrylic polymer prepared from acetoacetoxyalkyl (meth)acrylate
and an

alkene-containing component such as a polyfumarate, polymaleate,
a

polyester containing both fumarate and maleate groups or a
polyacrylate

comprises the reaction of a tertiary amine such as triethylene
diamine

and an ***epoxide*** such as a glycidyl-functional (meth)

acrylic
polymer in the presence of the methylene-containing component and
alkene-containing component. The tertiary amine can be
incorporated into
the alkene-containing component such as the reaction of an
unsaturated
polyester with a compound having both tertiary amine and primary
or
secondary amine groups. The tertiary amine can be incorporated
into the
methylene-containing component such as an acrylic polymer derived
from a
tertiary amino-functional monomer and acetoacetoxyalkyl (meth)
acrylate.

The ***epoxide*** can be incorporated into the methylene-
containing

component such as an acrylic polymer obtained from glycidyl
(meth)acrylate and acetoacetoxyalkyl (meth)acrylate. The

epoxide

can be incorporated into the alkene-containing component.

SUMM This invention relates to ambient cure compositions based on the
base-activated Carbon Michael reaction between active methylene

groups

and active alkene groups. More particularly, the invention is

directed

toward use of tertiary amines and ***epoxides*** to activate

the

Carbon Michael reaction. In more specific aspects, the invention

is

directed toward classes of active methylene groups, active alkene
groups, tertiary amines and ***epoxides*** that provide low

cost,

color and hazard, in two-pack coatings with good pot life, cure

speed,

gloss and durability on exposure to high humidity and ultraviolet

light.

Two-pack aliphatic urethane coatings represent the best current
technology and provide targets for pot life, cure speed, gloss

and

durability, but alternatives to urethanes are needed with

advantages in

economy, safety, and ease of handling, especially for coatings

with low

levels of volatile solvent.

SUMM It has been discovered that the pot-life/cure, cure rate/gloss
and

packaging problems with preferred alkene-containing and
methylene-containing components can be overcome by use of

tertiary

amines and ***epoxides*** as the main activator of Carbon

Michael

cure, with a key element being the occurrence of most of the

reaction

between tertiary amine and ***epoxide*** in the presence of

both the

activated alkene component and the activated methylene component.

Without limiting the scope of the invention, it is believed that

the

activation of Carbon Michael cure results from the conversion of

the tertiary amine to a quaternized nitrogen compound via reaction with the epoxy group in the presence of the Michael-reactive components. When tertiary amines are mixed with ***epoxides*** in the absence of Michael-reactive components the typical result is a complex mixture of quaternary ammonium compounds, their alkaline decomposition products, and polyether moieties from epoxy homopolymerization. It is believed that in the presence of activated methylene component the reaction between amine and ***epoxide*** forms quaternary ammonium salts with the weakly acidic methylene component, activating the methylene component for reaction with the alkene component.

SUMM Without limiting the scope of the invention, the pot-life/cure problem is believed overcome by two fundamental advantages of this method of activation. First, the pot-life is extended because the activator concentration starts at a low level, and second, the rate of formation of activator is greater in the film than in the pot because the concentrations of amine and ***epoxide*** increase due to loss of solvent.

SUMM Without limiting the scope of the invention, the cure-rate/gloss problem is believed overcome by the same mechanism as the pot-life/cure problem. The cure rate increases with time as activator is formed from reaction of amine and ***epoxide***, allowing solvent to leave the film while it is thermoplastic, yet giving a fast cure as sufficient levels of activator are formed.

SUMM Triethylenediamine does not give sufficient activation of Carbon Michael cure in the absence of ***epoxide***. However, in the presence of ***epoxide***, triethylenediamine gives faster activation than other tertiary amines, which is useful when a fast cure rate is needed.

SUMM When both the tertiary amine component and the ***epoxide*** component are low in molecular weight and not selected according to the preferred embodiments described below, films prepared using the invention tend to blister when exposed to water. This problem is overcome by a variety of solutions involving either the amine component or the ***epoxide*** component: (1) the amine can be

incorporated
into the active methylene component, for example by use of
acrylic
copolymers that contain both pendant acetoacetate moieties and
tertiary
amine from amine-containing monomers such as dimethylaminoethyl
methacrylate or dimethylaminopropyl methacrylamide; (2) the amine
can be
incorporated into the alkene component; (3) the ***epoxide***
can be
incorporated into the active methylene component, for example by
use of
acrylic copolymers that contain both pendant acetoacetate
moieties and
epoxide from copolymerization of glycidyl methacrylate,
or (4)
the ***epoxide*** can be incorporated into the alkene
component.

SUMM A preferred class of amine-containing active methylene components
is
derived from copolymerization of a monomer mixture containing
both
acetoacetate-functional and tertiary amine-functional monomers
such as
dimethylaminoethyl methacrylate or dimethylaminopropyl
methacrylamide.
The level of the tertiary amine-functional monomer is selected
according
to the level of the acrylic polymer in the binder, to provide,
along
with other amine components, the ratios of amine to
epoxide
specified below. The level of tertiary amine-functional monomer
then is
from about 2 percent by weight of total monomer for binders with
a high
level of acrylic to 15 percent for binders with a low level of
acrylic.

SUMM The preferred ***epoxide*** components contain the
epoxide
group as glycidyl esters, glycidyl ethers, or epoxidation
products of
alpha olefins. A preferred type for economy is the commercial
liquid
diglycidyl ether of bisphenol A, for example EPON 828 from Shell.
Other
types of ***epoxide*** give slower cure, presumably because
of their
slower reaction rate with tertiary amines. For best water
resistance,
especially with low molecular weight amine components, the
epoxide is incorporated in the Michael-reactive
methylene or
alkene component, for example by use of glycidyl methacrylate to
give
glycidyl esters in an acrylic copolymer containing pendant active
methylene moieties. However, for economy and ease of adjustment
of

epoxide level, one can use low molecular weight glycidyl esters, glycidyl ethers, or epoxidation products of alpha olefins. When using the low molecular weight ***epoxide*** components, for best water resistance it is preferred to use an amine component incorporated into the Michael-reactive methylene or alkene component, or capable of reaction with one of the Michael-reactive components during cure.

SUMM A preferred method for incorporation of the ***epoxide*** in the Michael-reactive methylene component is use of acrylic polymers containing pendant acetoacetate groups, incorporating ***epoxide*** by use of a monomer mixture containing glycidyl methacrylate along with acetoacetate-functional monomer. The level of glycidyl methacrylate in the acrylic polymer is selected according to the level of acrylic polymer in the binder, the level of any other acrylic or ***epoxide*** components, and the criteria for total ***epoxide*** level discussed below. With a high level of acrylic polymer and all of the acrylic polymer containing ***epoxide***, the glycidyl functional monomer may be as low as 4 percent in the acrylic polymer. When both an amine-functional acrylic and an epoxy-functional acrylic are used, the preferred level of glycidyl methacrylate may be 20 percent or more of the acrylic polymer with glycidyl and acetoacetate functionality.

SUMM There are three preferred ways to combine Carbon Michael-reactive, ***epoxide***, and amine components to achieve stable packages. The ***epoxide*** can be mixed prior to use with the active methylene moieties, the Carbon Michael-reactive alkene moieties, or a combination of the Michael-reactive components.

SUMM A particularly preferred method for achieving two packages of similar size is combination of the ***epoxide*** with either the active methylene moieties or the alkene moieties, and the tertiary amine with the other Carbon Michael-reactive component.

SUMM The ratio of total moles of tertiary amine groups to ***epoxide*** groups is not critical, but is usually from about 0.5 to about 1.5. Since the speed of cure increases with concentration of both amine and

epoxide groups, and the presence of an excess of amine is detrimental to acid resistance and weathering resistance, it is preferred to have the ratio of tertiary amine groups to ***epoxide*** groups from about 0.5 to about 1.0.

SUMM A useful statistic for the activator level is milliequivalents of ***epoxide*** per 100 grams of all activator and Carbon Michael

reactive components, based on non-volatile material. This gives a measure of the potential moles of strong base per total weight of binder. This number should exceed the level of acid in the binder by at least 2 milliequivalents/100 grams. When the binder contains low levels of acid, the preferred activator level is usually in the range 2-80 milliequivalents per 100 grams, and often in the range 10-40, with lower levels giving poor rate of cure and higher levels giving adverse effects on water or acid resistance.

SUMM The ***epoxide*** /tertiary amine activator can be supplemented by less than about 10 milliequivalents of preformed strong base per hundred grams of binder, with the strong base selected from the group consisting of salts of tetramethylguanidine, 1,8-diazabicyclo(5.4.0)undec-7-ene, or quaternary ammonium hydroxide with carbonic, acetic or hydrofluoric acids and mixtures thereof to accelerate cure. The level of strong base should be kept to the minimum level giving the desired improvement in early cure, due to adverse effects on water resistance. The carbonic salts give the best improvement of early surface cure, and are therefore usually preferred. This is thought to be due to the ease of loss of acid from the film as carbon dioxide. However, even at 10 milliequivalents per hundred grams of binder, the carbonic salts tend to give loss of gloss, and thick films can even wrinkle due to surface cure exceeding sub-surface cure and solvent loss.

SUMM Improvement of early cure without the problems of preformed base can be accomplished by use of phenols, or combinations of phenols and alcohols. Without limiting the scope of the invention, it is believed that phenols and alcohols accelerate the reaction between tertiary amines and ***epoxides***. Preferred phenols are alkylsubstituted, for

example

p(t-butyl)phenol and nonylphenol. Preferred levels of phenol are about 5 to about 30 milliequivalents per 100 grams total weight of activator plus Carbon Michael-reactive components. The alcohols are used at from 1 to 20 percent of the binder, with a preferred alcohol being 2-ethylhexanol.

SUMM With hydroxyl-terminated polyesters, hardness and chemical resistance can be improved by adding multifunctional isocyanate at the time of mixing Carbon Michael-reactive components, tertiary amine and ***epoxide***.

SUMM The invention also relates to coating or binder compositions including active methylene moieties, Michael-reactive alkene groups, ***epoxide*** groups, tertiary amines and supplementary additives for improvement of early cure.

DETD Three hundred twenty (320) grams of reagent grade xylene solvent was weighed into a one liter four neck flask. A monomer mix was prepared from 96 grams methyl methacrylate, 96 grams butyl methacrylate, 96 grams styrene, 192 grams AAEM, and 7.2 grams of t-butyl peroctoate. A solution of n-dodecyl ***mercaptan*** was prepared by dissolving 12.1 grams of the ***mercaptan*** in enough of the solvent to make 60 ml of solution. The remaining solvent was stirred with a nitrogen sparge and heated to 105 degrees C. The monomer mix and ***mercaptan*** solution were then added simultaneously over a period of 95 minutes at 103-106 degrees C. Following completion of the additions the mixture was held at 105 degrees C. for another 150 minutes with 2 gram portions of t-butyl peroctoate being added after 45 and 95 minutes. The resulting 816 grams of solution was found to contain 60.9 wt. % polymer solids. Gel permeation chromatography indicated that the molecular weights were Mw=15,200, Mn=5560. The monomer ratio was 40 AAEM/20 MMA/20 BMA/20 Styrene. The initiator was 1.5% t-butyl peroctoate on polymer solids. The chain regulator was 2.5% n-dodecyl ***mercaptan*** on polymer solids.

DETD Polymer B was prepared by the same procedure used with Polymer A, except

for use of 1.5% 2,2'-azobis(2-methylbutanenitrile) as the initiator in place of t-butyl peroctoate, and use of 5.0% n-dodecyl ***mercaptan*** in place of 2.5%. Gel permeation chromatography indicated that the molecular weights were Mw=8170, Mn=2720.

DETD AAEM copolymers were prepared as described above except no ***mercaptan*** was used, the initiator was 2.16 wt. % t-butyl peroctoate on monomers, and the monomer compositions were as follows:

DETD TABLE 3

Hardness development with only epoxy/amine latent catalyst.
Knoop Hardness

Epoxy Identification	14		
Chemical Composition			
	1 day	8 day	day
Araldite RD-1			
Butyl Glycidyl Ether	0.32	0.69	0.82
Araldite CY-179			
Cycloaliphatic Diepoxide	0.38	0.52	0.59
Araldite DY-025			
C-12/C-14 Alkyl Glycidyl Ether tacky	5.77	9.90	
Araldite DY-027			
C-8/C-10 Alkyl Glycidyl Ether	0.36	3.28	7.06
Araldite MY-720			
N-Tetraglycidylmethylenbis-benzenamine	0.34	1.54	5.72
Araldite Resin			
4-Glycidylloxy-N,N-di-Glycidyl	0.32	5.20	9.65
500 aniline			
Araldite Resin			
Same as Resin 500	0.38	4.54	9.72
510			
Heloxy MK-116			
2-Ethylhexyl Diglycidyl Ether	0.36	4.38	9.24
Heloxy WC-67			
1,4- ***Butanediol*** Diglycidyl Ether	0.32	9.54	12.55
Heloxy WC-68			
Neopentylglycol Diglycidyl	0.33	9.18	11.85
Ether			
Heloxy MK-107			
Cyclohexyldimethanol Diglyc.	0.32	8.86	12.35
Ether			
Heloxy WC-69			

	Resorcinol Diglycidyl Ether	0.31	9.80	13.00
Heloxy WC-84	Aliphatic Polyol Di/Triglyc.			
	tacky	2.88	5.97	
Epon 828	Ether Bisphenol A Digylcidyl Ether	0.39	9.82	14.40

DETD	TABLE 4
------	---------

—
Evaluation of TEDA and DMAM as tertiary amine for latent catalyst system with ***epoxides*** .

Amine	Epoxy	Gel 500 g	Knoop	Pencil
				Butyl
Level	Level			
	Time			
		Zapon	Hardness	
			Hardness	
			Acetate	
Amine (meq/100 grams)				
	(Hrs)			
	(Minutes)			
		1 day		
		14 day		
		14 day		
			Patch	

—
Enamels using AAEM copolymer without copolymerized amine.

DMAM	21	21	>120		
			344-382		
			0.36		
			9.97		
			F	<6B	
DMAM	42	42	>120		
			514-1419		
			0.76		
			15.50		
			H	<6B	
DMAM	63	63	98-120		
			521-1416		
			1.76		
			13.95		
			H	HB	
DMAM	42	84	98-120		
			518-1409		
			1.20		
			13.1		
			H	HB	
DMAM	42	126	76-98		
			514-1405		
			1.52		
			12.35		
			H	HB	
DMAM	21	63	>120		
			511-1406		
			0.58		

				11.10		
				F	<6B	
TEDA	21	21	10-24			
			180-274			
			3.72			
			13.33			
				F	No Film	
TEDA	42	42	<5 172-270			
			5.52			
			12.75			
				F	<6B	
TEDA	63	63	<5 173-267			
			6.74			
			12.65			
				H	B	
TEDA	42	84	<5 312-348			
			3.49			
			13.27			
				H	<6B	
TEDA	42	126	<5 161-266			
			2.06			
			7.95			
				F	<6B	
TEDA	21	63	<5 408-456			
			1.99			
			8.36			
				F	<6B	
Enamel using AAEM copolymer with copolymerized amine.						
DMPMA						
	21	21	>120			
			404-452			
			0.33			
			11.43			
				H	<6B	

DET D The AAEM copolymers were prepared without ***mercaptan*** chain transfer agent, with the following monomer compositions and molecular weights (Mw/Mn) indicated by gel permeation chromatography:

DET D TABLE 6

Blue paint comparison of activation by tetrabutylammonium bicarbonate and by ***epoxide*** /tertiary amine with polyester as alkene component.

AAEM Copolymer F/G (1/1) H

Additive	TEDA	TBACARB
Blueness	Deep	Pale
Knoop Hardness at 1 day		
	1.6	1.3
Knoop Hardness at 4 days		
	4.5	1.5
Knoop Hardness at 14 days		
	8.9	2.4
Pencil Hardness at 1/4/14 days		
	B/F/H	B/B/B
Swell ratio at 4/14 days		

	1.73/1.55	2.04/2.00
Direct Impact (in-lb) at 14 days	70-90	50-70
20 degree gloss at 14 days	81.2	66.0

DETD

TABLE 7

Blue paint comparison of activation by tetrabutylammonium bicarbonate and by ***epoxide*** /tertiary amine with TMPAOPA as alkene component.

AAEM Copolymer	F/G (1/1)	H
Additive	TEDA	TBACARB
Blueness	Nearly Deep	Pale
Knoop Hardness at 1 day	4.1	1.3
" 4 days	7.2	1.8
" 14 days	10.0	2.7
Pencil Hardness at 1/4/14 days	F/F/H	F/HB/HB
Swell ratio at 4/14 days	1.41/1.34	1.58/1.54
Direct Impact (in-lb) at 14 days	70-90	>130
20 degree gloss at 14 days	82.9	79.1

DETD Direct Comparison of Epoxy/Amine and Preformed Strong Base Activators
Using the Same AAEM Copolymer with Both Activators, and Demonstration of Advantages in Water Resistance with TEDA when the Epoxy Component is an AAEM/GMA Copolymer Rather than a Low Molecular Weight ***Epoxide***

DETD Pigment dispersions were prepared with titanium dioxide as sole pigment, using a sand grind procedure with AAEM copolymers as vehicle. The AAEM copolymers were prepared without ***mercaptan***, using t-butyl peroctoate as initiator with 4.5 or 9.0 weight percent t-butyl peroctoate based on monomers. The monomer composition was 40 AAEM/52 i-BMA/8 GMA. AAEM copolymer L, prepared with 9.0 percent t-butyl peroctoate, had Mw=9,960, Mn=2760. AAEM copolymer M, prepared with 4.5 percent t-butyl peroctoate, had Mw=20,700, Mn=6910.

DETD White paints were prepared as described in Example 25, using AAEM Copolymer N and either TMPAOPATE or the repeat of Polyester C described in Example 25. The binder composition for each paint contained a total of 9.15 grams AAEM copolymer plus alkene component (TMPAOPATE or Polyester C). The remainder was 0.6 grams Epon 828 and 0.25 grams bis-DMAPA. All paints also contained 0.2 grams p-t-butyl phenol

and 0.01

grams Silicone SF-1023, with xylene as solvent. AAEM copolymer N was prepared with monomer composition 40 AAEM/55 i-BMA/5 Styrene, 1 weight percent 2,2'-azobis(2-methylbutanenitrile as initiator and 1% n-dodecyl ***mercaptan***, and had Mw/Mn=21,900/9220.

CLM What is claimed is:

1. A method for reacting a methylene-containing component and an alkene-containing component comprising mixing and reacting a tertiary amine and an ***epoxide*** in the presence of the methylene-containing component and the alkene-containing component wherein the tertiary amine is selected from the group consisting of a tertiary amino-functional acrylic polymer; a tertiary amino-functional polyester; triethylenediamine; a compound containing both tertiary amine and primary or secondary amine; a Mannich reaction product of a secondary amine, formaldehyde and a phenol; and mixtures thereof.

CLM What is claimed is:

11. The method according to claim 1 wherein the ***epoxide*** is selected from the group consisting of a mono- and poly-functional glycidyl compound, a polyepoxide derived from an alpha-olefin and mixtures thereof.

CLM What is claimed is:

18. The method according to claim 1 wherein the ***epoxide*** is a glycidyl-functional acrylic polymer and the tertiary amine is triethylenediamine.

CLM What is claimed is:

19. The method according to claim 1 wherein the ***epoxide*** is selected from the group consisting of a mono-, di- and tri-functional glycidyl compound and a polyepoxide of an alpha olefin, and the tertiary amine is selected from the group consisting of a tertiary amino-functional acrylic polymer, a tertiary amino-functional polyester, a compound having both a tertiary amine and a primary or secondary amine, and mixtures thereof.

IT 62-49-7 ***280-57-9***, 1,4-Diazabicyclo[2.2.2]octane 2052-49-5,

Tetrabutylammonium hydroxide 17351-62-1
(catalysts, coatings of methylene polymers, alkene polymers, and epoxides contg., for fast curing)

=>

---Logging off of STN---

=>

Executing the logoff script...

=> LOG Y

COST IN U.S. DOLLARS	SINCE FILE	TOTAL
	ENTRY	SESSION
FULL ESTIMATED COST	85.61	103.37

STN INTERNATIONAL LOGOFF AT 14:33:00 ON 05 DEC 2009